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Volume 1. Results and Discussion

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OUTDOOR CHAMBER STUDY TO TEST MULTI-DAY EFFECTS

VOLUME I. RESULTS AND DISCUSSION

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The smog chamber facilities of the University of California, Riverside were used to collect experimental data to assess the effects of multi-day irradiations on photochemical oxidant formation. Two chambers were used during this program: a 6,400-ℓ indoor Teflon chamber with blacklight irradiation and a 50,000-ℓ dual-mode outdoor Teflon chamber that used natural sunlight as the light source. A total of 28 indoor and 55 outdoor chamber experiments were completed in this study. In this volume, the experimental facility, methods of procedure and analytical techniques are described and the results are summarized and discussed. The data obtained are suitable for use in developing and testing kinetic mechanisms of photochemical smog formation.

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ABSTRACT

A series of single- and multi-day indoor and outdoor environmental chamber experiments have been carried out at the Statewide Air Pollution Research Center (SAPRC) at the University of California in Riverside to derive data suitable for testing chemical models for multi-day photochemical air pollution episodes. Two environmental chambers were used during this program, a ~6400-ℓ indoor Teflon chamber with blacklight irradiation and a ~50,000-ℓ dual-mode outdoor Teflon chamber which employed natural sunlight as the light source. A total of 32 indoor and 55 outdoor chamber experiments were completed during this program. These chamber experiments consisted primarily of multi-day NO_x-air irradiations of an eight-component hydrocarbon surrogate designed to represent emissions of reactive organics into urban atmospheres from all sources, and associated control and characterization runs. Most of the multi-day surrogate-NO_x-air experiments in the outdoor chamber were run with the chamber in the dual mode, where each experiment consisted of simultaneous irradiation of two different mixtures under the same temperature and lighting conditions. In addition, an isobutene-NO_x-air irradiation was carried out in the indoor chamber to test chemical computer models for the NO_x-air reactions of this surrogate component.

Problems with side inequivalency in the dual-mode outdoor chamber experiments were encountered in preliminary experiments carried out in 1982. These were subsequently resolved, and good side-to-side equivalency was obtained in the experiments carried out in 1983. During that time, irradiations of a "standard" surrogate-NO_x-air mixture were carried out under a variety of temperature and light intensity conditions, allowing the combined effects of these to be determined. Good reproducibility of experiments carried out under similar weather conditions was observed.

The multi-day surrogate-NO_x-air irradiations were carried out in both chambers at a variety of initial hydrocarbon and NO_x concentrations. In general, it was found that runs which were less reactive on the first day with respect to O_3 formation tended to be more reactive on subsequent days, and vice versa. This resulted in the maximum O_3 levels in multi-day runs being much less dependent on initial reactant concentrations than expected based on results of single-day irradiations.

The data obtained during this program are presented in three volumes, of which this is Volume I. In this volume, the experimental facility, methods of procedure, and analytical techniques are described, and the results are summarized and discussed. Volume II contains printouts of the detailed data from these experiments and Volume III contains the data in computer-readable format. These volumes are submitted in fulfillment of Cooperative Agreement No. CR810260-01 for the U. S. Environmental Protection Agency, which covers the period from August 11, 1982 through August 10, 1984.

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SECTION I

INTRODUCTION

During the last decade, there have been significant advances in our understanding of the chemistry occurring in photochemical air pollution (Demerjian et al. 1974, Finlayson and Pitts 1976, Finlayson-Pitts and Pitts 1977, Herron et al. 1979, Atkinson and Lloyd 1984). A progressive development of detailed chemical models for the simple alkanes, alkenes and aromatics (Niki et al. 1972, Demerjian et al. 1974, Hecht et al. 1974, Hendry et al. 1978, Falls and Seinfeld 1978, Carter et al. 1979, Whitten et al. 1979, 1980a,b, Atkinson et al. 1980, Atkinson and Lloyd 1984), which have been tested against environmental chamber data has occurred during this time period. While these chemical models, in abbreviated, cut-back, or "lumped" forms have been, and are being, used in airshed computer models (for example, Reynolds et al. 1974, McRae at al. 1979, Atkinson et al. 1982), these chemical models have only been validated for, and thus are only applicable to, single-day conditions.

For most major urban airsheds, especially those in the eastern and northeastern United States and the California South Coast Air Basin, multi-day episodes are the rule, rather than the exception, and hence airshed models must incorporate chemical packages designed specifically for such conditions. Since the development of a chemical model requires the availability of environmental chamber data against which it can be tested, there is a need for fully characterized multi-day environmental chamber data. Thus the Environmental Sciences Research Laboratory of the U. S. Environmental Protection Agency contracted to the Statewide Air Pollution Research Center (SAPRC) at the University of California, Riverside, to conduct a series of indoor and outdoor chamber experiments simulating multi-day conditions using hydrocarbon and NO_x mixtures designed to simulate those present in urban airsheds. The results of this experimental program, together with a discussion of the environmental chambers, experimental conditions and analytical techniques employed, are presented in this report.

Two different environmental chambers were employed in this program: a ~50,000-ℓ outdoor all-Teflon chamber and a ~6400-ℓ indoor all-Teflon chamber. Both chambers were employed because each has its own unique set of advantages. The outdoor chamber has a lower surface/volume ratio and has more realistic lighting conditions, while indoor chamber experiments can be carried out under more controlled conditions. Thus the indoor and outdoor chamber experiments are seen as complementary, to allow more thorough and comprehensive testing of the chemical models.

Both environmental chambers employed in this program were constructed from replaceable FEP Teflon film which could collapse as samples were withdrawn for analysis, thus avoiding dilution of their contents during the experiments. The ~50,000-ℓ outdoor chamber could be operated in either single or dual mode. The majority of the experiments conducted in this outdoor chamber on this program were carried out in the dual mode, and hence two separate experiments could be simultaneously run with the same lighting and temperature conditions. The indoor chamber was operated solely in the single mode. However, since the light intensity and temperature could be held constant in this chamber and thus reproduced from run to run, dual mode capability for this chamber was not necessary. The design and characteristics of these chambers are discussed in detail in Section II.

The principal experimental runs in this program consisted of multi-day irradiations of "urban surrogate"-NO_x-air mixtures. The "urban surrogate" consisted of a mixture of eight hydrocarbons chosen to simulate emissions into urban atmospheres (Whitten and Killus, private communication), with a composition given in Table 1. The "standard" reactant mixture consisted of ~4 parts-per-million of carbon (ppmC) of this surrogate mix together with ~0.4 ppm of NO_x (at an initial $[NO]/[NO_2]$ ratio of ~2), although experiments were also carried out with differing surrogate and NO_x concentrations to investigate the effects of varying the initial reactant concentrations. Isobutene was included in the surrogate mixture primarily to represent formaldehyde, which is an important constituent of urban emissions. Isobutene reacts rapidly to form formaldehyde (along with acetone) in NO_x-air photooxidations. This was confirmed in a separate isobutene-NO_x-air irradiation carried out under this program. Formaldehyde itself was not included in the reaction mixture due to difficulties in handling it, nor were other aldehydes included since they were found to be difficult to reproducibly inject in our chambers with the techniques available (Atkinson et al. 1983). In addition, dry air (<10%

Table 1. Composition[a] of the "Urban Surrogate" Hydrocarbon Mixture

Hydrocarbon	% Carbon	ppm Component / ppmC Surrogate
Ethene	5.0	0.025
Propene	5.6	0.019
Isobutene	14.3	0.036
n-Butane	15.8	0.040
n-Pentane	19.6	0.039
Isooctane	14.8	0.018
Toluene	12.6	0.018
m-Xylene	12.3	0.015

[a] Based on analyses of cylinder gases employed in outdoor chamber experiments carried out in 1983. The average composition of surrogate employed in the indoor chamber experiments and the earlier outdoor runs, where each individual component was injected separately, was similar.

RH) was employed in all outdoor irradiations in order to avoid condensation of water on the chamber walls and formaldehyde absorption and degassing, which were found to be a problem in University of North Carolina outdoor chamber runs carried out at higher humidities (Whitten and Killus, private communication).

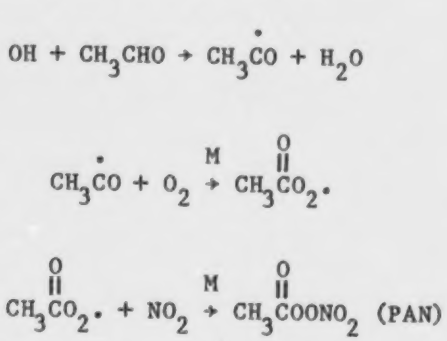
The surrogate-NO_x-air irradiations were of two to four days duration each, with NO_x being injected on subsequent days in some experiments to simulate NO_x emission into an aged air mass, and to allow renewed photochemical O_3 production, so the maximum O_3 formation potential of the partially reacted surrogate mixture could be determined. The majority of the experiments were carried out to determine the effects of varying the initial reactant concentrations, with (in the case of the dual-mode outdoor experiments) a "standard" surrogate-NO_x-air mixture being irradiated on one side of the chamber, and a mixture with differing initial surrogate and/or NO_x concentrations on the other. Thus for the outdoor runs, a number of repeats of the "standard" surrogate-NO_x-air run were carried out, allowing the reproducibility of these runs to be assessed, and giving some indication of how the results of these runs were affected by differences in ambient temperature and light intensity. As expected, good reproducibility in the standard surrogate-NO_x-air runs carried out in the indoor chamber was observed, and hence a large number of such runs in that chamber was not necessary.

In addition to the multi-day surrogate-NO_x-air irradiations, a number of conditioning, control and characterization runs were carried out in both chambers in order for the experimental runs to be of maximum utility for model testing purposes. In particular, the experimental program included the following types of runs:

(1) Propene-NO_x-air irradiations were carried out to condition new reaction chambers and to recondition outdoor chambers which had been used in dual chamber runs with differing mixtures, or which exhibited side inequivalency. These runs were also useful for control purposes since the chemistry of irradiated NO_x-propene-air mixtures is reasonably well understood, and can be used to test the representations of chamber effects and lighting conditions in the chemical models. Typically, initial concentrations of ~1 ppm of propene and ~0.5 ppm of NO_x were employed in these runs.

(2) Ozone conditioning experiments were carried out both to condition new reactors and to measure the O_3 dark decay rates in new or used reaction chambers.

(3) Acetaldehyde-air irradiations were carried out to measure the rate of NO_x offgassing in both new and used reaction chambers, and to measure the rate of NO_x offgassing on the second day in some multi-day runs. The atmospheric photooxidation of acetaldehyde results in the formation of acetylperoxy radicals, which then react with NO_2 emitted from the walls to form peroxyacetyl nitrate (PAN)



$$OH + CH_3CHO \rightarrow CH_3\dot{C}O + H_2O$$

$$CH_3\dot{C}O + O_2 \xrightarrow{M} CH_3\overset{\overset{O}{\|}}{C}O_2\cdot$$

$$CH_3\overset{\overset{O}{\|}}{C}O_2\cdot + NO_2 \xrightarrow{M} CH_3\overset{\overset{O}{\|}}{C}OONO_2 \text{ (PAN)}$$

with the rate of formation of PAN thus reflecting the NO_x emission rates. Typically, an initial concentration of 0.5 ppm of acetaldehyde was used in these experiments.

(4) Tracer-NO_x-air or CO-tracer-NO_x-air irradiations were conducted to measure the background chamber radical source. These irradiations were also useful in measuring offgassing of contaminants such as reactive organics which convert NO to NO_2. Chamber radical sources, and the utility of these types of experiments in measuring them, have been discussed in detail previously (Carter et al. 1981, 1982). The experiments consisted of irradiations of ~0.4 ppm NO_x and ~10 ppb each of propene and n-butane tracers [to monitor OH radicals from their relative rates of decay (Carter et al. 1981, 1982)] with or without ~50 ppm of CO. Typically, in the outdoor chamber dual-mode experiments, a tracer-NO_x-air experiment was carried out on one side while a CO-tracer-NO_x-air run was simultaneously carried out on the other. In the indoor chamber these runs were carried out sequentially, with the CO being added at the end of a tracer-NO_x-air irradiation for the purpose of carrying out the CO-tracer-NO_x-air run.

(5) For the outdoor chamber in dual-mode configuration, experiments were carried out in which an identical mixture was irradiated in each side to determine to what extent the sides were equivalent. Mixtures employed were usually the "standard" urban surrogate-NO_x-air mixture, although occasionally propene-NO_x-air mixtures were also employed. Side inequivalency was found to be a problem during the first phase of this program (see below), and thus a large number of such experiments were conducted during that period.

The experimental program discussed in this report was carried out in four phases. The first phase consisted of a preliminary set of outdoor chamber experiments carried out during the fall and early winter of 1982. During this phase of the program serious problems with side inequivalency in dual-mode runs were encountered. Thus most experiments conducted during this phase consisted of side equivalency tests (as described above) and of various conditioning and other procedures aimed at removing or at least elucidating the source of this inequivalency. The second phase of this program consisted of the indoor chamber experiments which were carried out during the winter and spring of 1983, and a total of six surrogate-NO_x multi-day runs, two irradiations employing ambient air, and 24 associated conditioning and characterization runs were successfully completed. The third phase of this program consisted of the outdoor chamber runs carried out during the summer and fall of 1983. In contrast to the first phase, no significant problems with side inequivalency in dual-mode chamber runs carried out during the third phase were encountered, and a total of 11 surrogate-NO_x-air multi-day runs, of which all but one were dual-chamber runs, and 11 conditioning and characterization runs were successfully completed during this phase of the program.

The fourth and final phase of this program consisted of an isobutene-NO_x-air irradiation carried out in the indoor Teflon chamber, together with a total of seven characterization and control runs.

This report consists of three volumes. In Volume I, the experimental facilities and procedures and the analytical techniques employed in all four phases of this program are described and the results of all experiments are summarized. The detailed tabulation of the data obtained from these experiments is given in Volume II of this report. These include not only measured concentration-time data and other measured parameters, but also comments giving specific procedures and observations made by the operators during the experiment. These data are also available in computer readable format on magnetic tape, and this tape, along with a description of the format of its data sets, comprises Volume III of this report. Although detailed interpretations of the results of these experiments were not within the scope of this program, some general observations concerning the results of these experiments are also presented in this volume of this report.

SECTION II

EXPERIMENTAL

A. Outdoor Chamber Irradiations

1. Chamber and Facility

The outdoor chamber experiments were carried out using the SAPRC outdoor Teflon bag chamber shown schematically in Figure 1. The reaction chamber consisted of a replaceable 45,000- to 60,000-ℓ bag which was constructed of 2 mil thick FEP Teflon sheets heat-sealed together using a double lap seam and externally reinforced with Mylar tape. Each bag used nine 30-ft x 60-in. Teflon panels. As shown in Figure 1, there were three Teflon injection or sampling ports on each side of the bag, one for manifold sampling, a second for filling and injecting and a third for gas chromatographic sampling and formaldehyde sampling. Two opposite corners of the bag were not heat-sealed and were used to empty the bag. During the experiments, these were held tightly shut with specially designed metal clamps. As indicated in the data summaries given in the following section, several different Teflon reaction chambers were used during this program.

The Teflon chambers were supported by plastic-coated wire running across a 20-ft x 20-ft cast-iron pipe frame held three feet off the ground to allow air circulation under the chamber. No mechanical stirring devices were used in these experiments. Rather, the reactants were mixed after injection by manual agitation of the sides of the flexible chamber. Wind action on the chamber and temperature gradients within the chamber were sufficient to ensure adequate mixing during an experiment. The chamber was held on the frame with a net connected to the frame by a system of ropes (only partially shown in Figure 1). Between irradiations and during dark decay experiments, the framework above the bag was covered by an opaque, white cover made of L-16 tarp material which was pulled on or off the framework by a system of rollers.

The majority of the analytical monitoring instruments employed were housed in an air conditioned 15-ft x 10-ft portable building sited approximately 10 feet from the chamber. The sample lines were constructed of 0.5-in. o.d. FEP Teflon tubing, and were connected to the sample ports on each side of the chamber (see Figure 1). The Teflon tubing from each

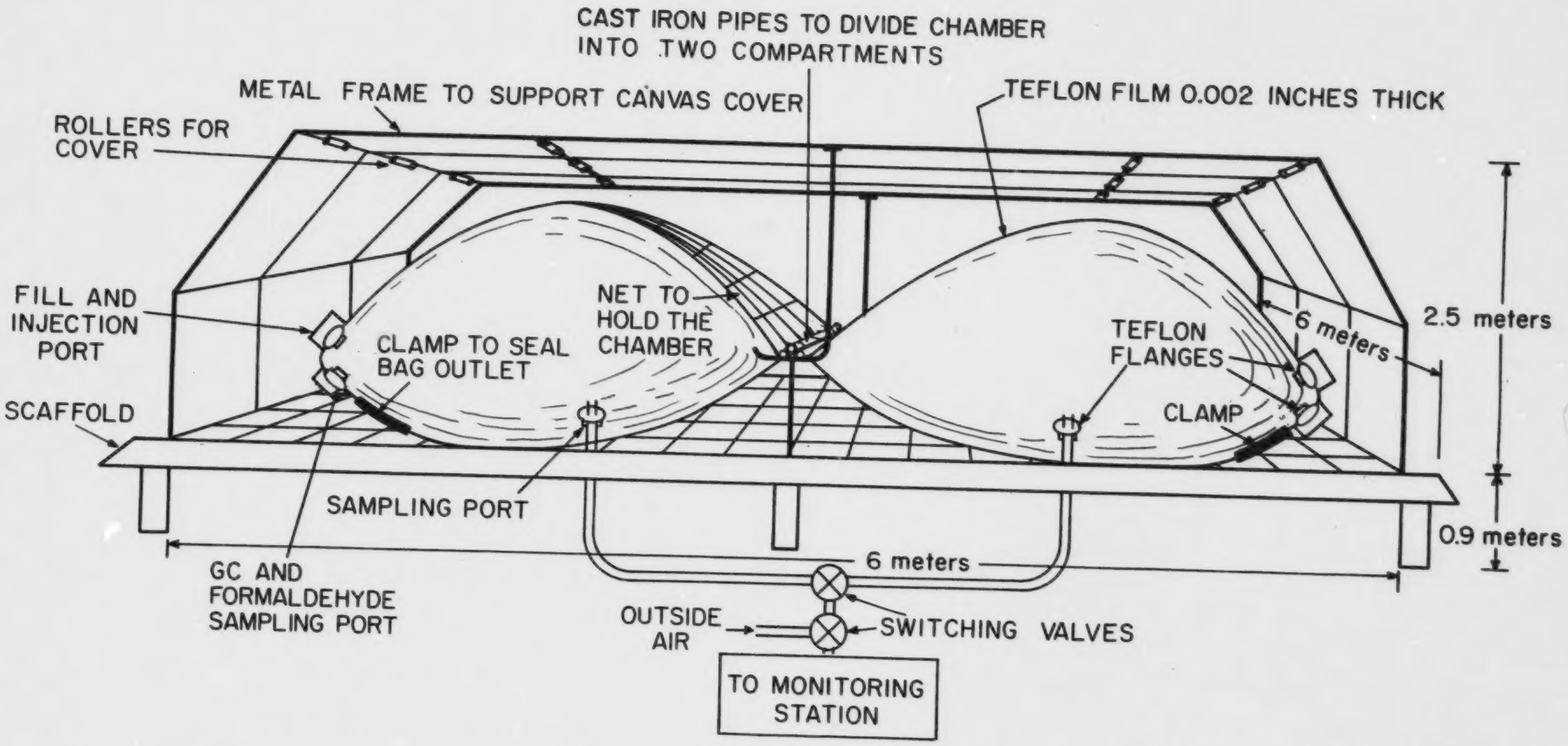

CAST IRON PIPES TO DIVIDE CHAMBER INTO TWO COMPARTMENTS
METAL FRAME TO SUPPORT CANVAS COVER
TEFLON FILM 0.002 INCHES THICK
ROLLERS FOR COVER
FILL AND INJECTION PORT
NET TO HOLD THE CHAMBER
CLAMP TO SEAL BAG OUTLET
TEFLON FLANGES
6 meters
2.5 meters
SCAFFOLD
CLAMP
SAMPLING PORT
0.9 meters
6 meters
GC AND FORMALDEHYDE SAMPLING PORT
OUTSIDE AIR
SWITCHING VALVES
TO MONITORING STATION

Figure 1. SAPRC outdoor Teflon chamber shown in dual-mode configuration.

side of the chamber was attached to an all-Teflon solenoid valve, with 0.5-in. orifices, which selected the side from which the sample was taken. This valve was attached, via Teflon tubing, to a similar valve which selected whether the sample was drawn from the Teflon chamber or from ambient air. After these valves, the sample lines led into a glass sampling manifold within the monitoring station to which the continuous analyzers were attached. The total air flow through the manifold was approximately 3.7 ℓ min^{-1}, and the transit time from the chamber to the manifold was approximately five seconds.

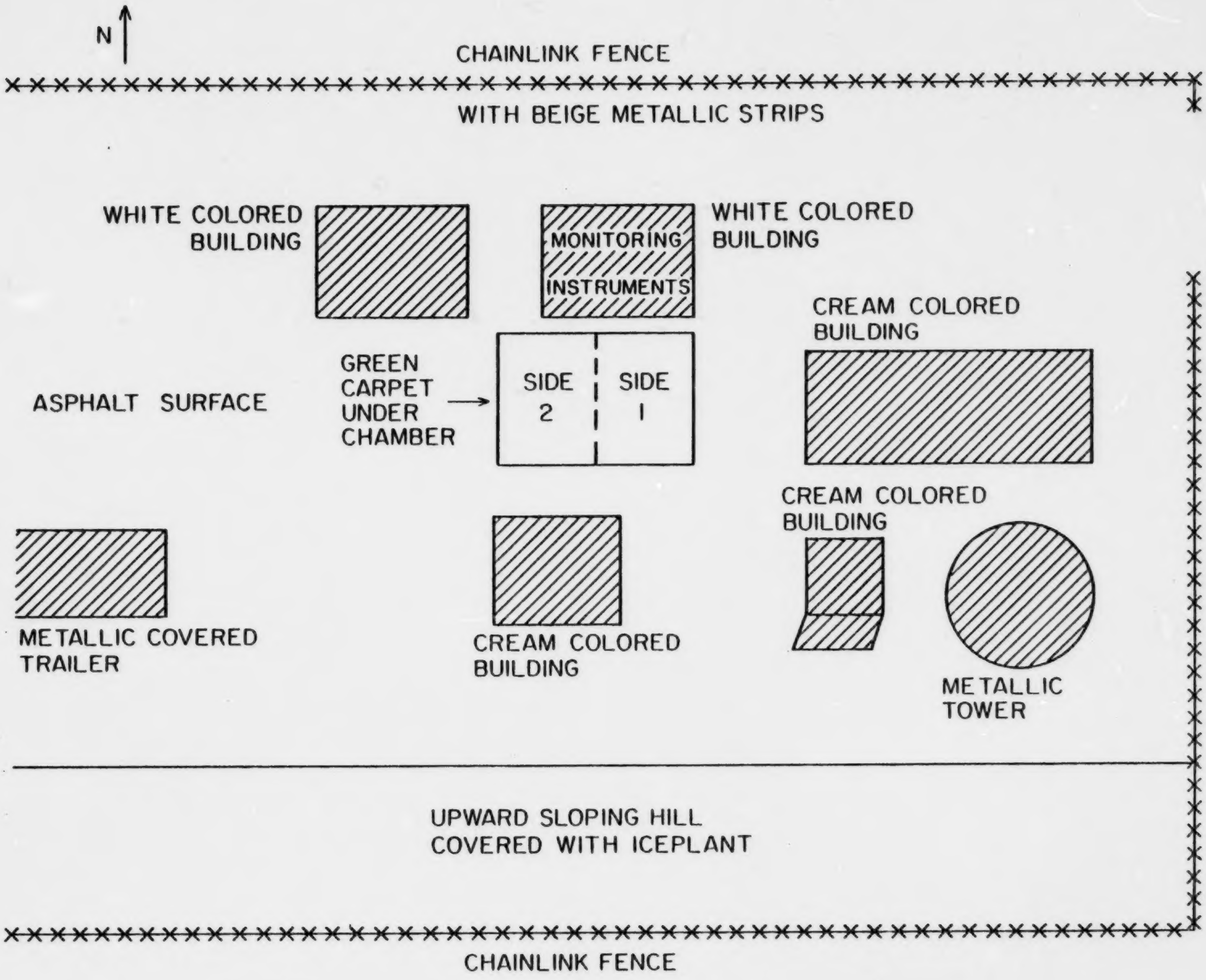
The switching valves which selected the source of air into the sampling manifold were controlled by an Apple II microcomputer which was also used to collect the data from the continuous monitoring instruments. For experiments during daylight hours, sampling was carried out on a 30-minute cycle, with samples being drawn for 10 minutes alternately from each side of the chamber and from the ambient air (the latter designated "side 3" on the data sheets in Volume II and the data sets in Volume III). During nighttime hours, however, in order to minimize the volume of air withdrawn from the bag, sampling was carried out on a 60-minute cycle with the valves being switched to draw sample gases from each side of the chamber for 10 minutes each, and then to withdraw sample from ambient air for 40 minutes. Data were not collected by the computer until six minutes after the valves were switched, and the signals from the instruments were then averaged for four minutes. These data were printed and stored on a diskette for later transfer to a central campus computer for processing.

As shown in Figure 1, the outdoor chamber could be operated in a dual mode configuration in order to conduct parallel experiments under the same lighting and temperature conditions. This division of the entire chamber was carried out by means of three 1.4-in. diameter cast-iron pipes. The bag was divided by raising the lower pipe and placing it tightly between the upper pipes, and then rotating them by 180 degrees, thus forming the seal. Previous data have shown that this procedure resulted in an exchange rate between the chamber sides of <0.1% per hour (Carter et al. 1981).

Dry ($\lesssim$5% RH), pure air for filling and flushing the chamber was supplied by an Aadco 737-15 air purification system which could generate an air flow of 250 $\ell\ \mathrm{min}^{-1}$. However, this system was not operational for some experiments; in those cases, the chamber was filled with relatively unpolluted morning air using a fan. Background samples from the chamber filled from the output air from the AadCo air purification system indicated negligible contamination by oxides of nitrogen or organics, and contamination was also relatively minor for most runs using ambient air. The data sheets and data sets in Volumes II and III, and the data summaries in Section III of this volume indicate which experiments used ambient air. In addition, the data sheets and data sets in Volumes II and III indicate the dew point depression measured during the experiments, from which the humidity can be calculated (but see Disucssion in Section II-C-3).

The geographical orientation of the chamber and its relationship to surrounding structures at the time of the initial series of outdoor chamber experiments is indicated in Figure 2. None of these structures was sufficiently close or tall to cast direct shadows on the chamber during the experimental runs, but they are shown because they affected reflected light and may have contributed to the side inequivalency problems observed during the first phase of these experiments (see Section III.A.6). Around the end of the first series of outdoor runs, the chamber was moved 30 feet to the west, and between the time of the first and second series of outdoor runs, some modifications were made to the structures around the chamber. The final configuration as used during 1983 is shown in Figure 3. For both phases of the outdoor chamber program, the grounds around the chamber were surfaced with asphalt, except immediately under the chamber where it was covered with a green indoor-outdoor carpet.

As seen from Figures 2 and 3, during both phases of the outdoor experiments the chamber was usually oriented so that the pipes dividing the bag were in a north-south orientation. By convention, side 1 always refers to the eastern half of the chamber when the framework was in this orientation, regardless of which particular half of the chamber was on the eastern side. (This is to avoid ambiguity since the chamber was rotated by 180° relative to the framework in some of the side equivalency t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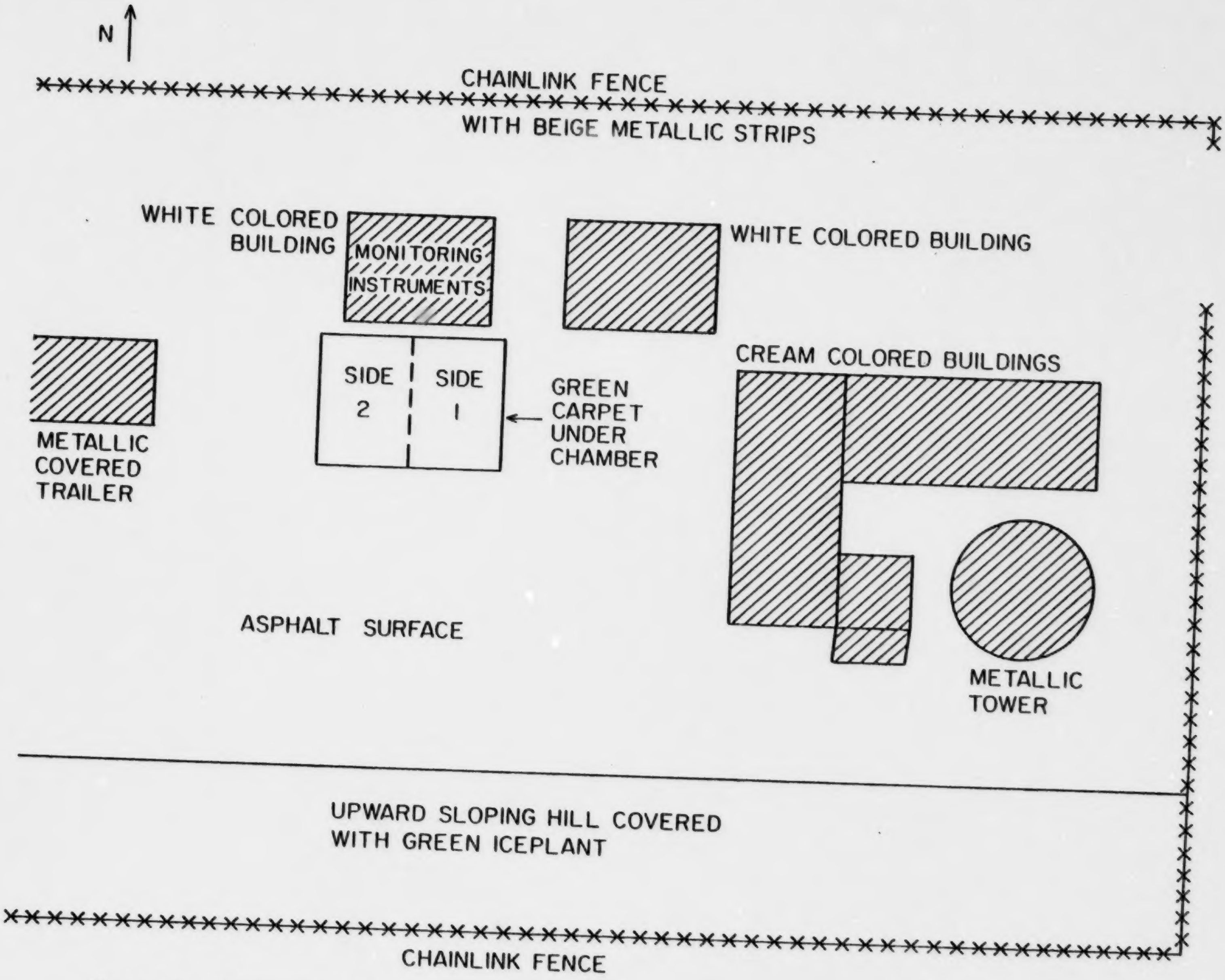
GREEN CARPET UNDER CHAMBER
SIDE 2
SIDE 1
CREAM COLORED BUILDING
METALLIC COVERED TRAILER
CREAM COLORED BUILDING
METALLIC TOWER
UPWARD SLOPING HILL COVERED WITH ICEPLANT
CHAINLINK FENCE

Figure 2. Geographical orientation of the outdoor chamber and surrounding structures at the time of the outdoor chamber experiments carried out in 1982.



N
CHAINLINK FENCE
WITH BEIGE METALLIC STRIPS
WHITE COLORED BUILDING
MONITORING INSTRUMENTS
WHITE COLORED BUILDING
METALLIC COVERED TRAILER
SIDE 2
SIDE 1
GREEN CARPET UNDER CHAMBER
CREAM COLORED BUILDINGS
METALLIC TOWER
ASPHALT SURFACE
UPWARD SLOPING HILL COVERED
WITH GREEN ICEPLANT
CHAINLINK FENCE

Figure 3. Geographical orientation of the outdoor chamber and surrounding structures at the time of the outdoor experiments carried out in 1983.

conducted during the first phase of the program.) In a few experiments during the first phase, the framework was rotated by 90°, with side 1 being defined as the south side. However, this orientation was not used in any of the experiments in the second series of outdoor runs. The data summaries in Section III (and the detailed tabulations in Volumes II and III) indicate which experiments were carried out with the chamber configuration or environment different than as indicated in Figure 2 or 3.

2. Experimental Procedures

The chamber was filled with dry, pure air in the morning immediately before the run began, and, in order to determine background levels, samples were analyzed using all of the gas chromatographic instruments prior to injection of the reactants. Following this any reactants whose initial concentrations were the same on both sides were injected, prior to separating the sides.

The reactants were injected into the chamber using several methods, depending on the reactant and, for the surrogate components, whether it was the first or second series of runs. In the case of NO, the calculated volume of gaseous NO was taken from a cylinder of Matheson, C.P. grade nitric oxide with a 20-mℓ gas-tight, all-glass, syringe (with stainless steel tip). This NO was then diluted to 100 mℓ with Liquid Carbonic Hi-Pure nitrogen in a separate 100-mℓ, gas-tight, all-glass syringe. The NO_2 injection was prepared in a similar manner, except that the NO was diluted with Liquid Carbonic Industrial Grade oxygen for $\gtrsim 5$ mins to yield NO_2. Introduction of both of these compounds into the chamber was accomplished by means of 5-ℓ glass bulbs with a straight bore Teflon stopcock at one end, and a "T"-bore Teflon stopcock at the other end. The bulbs were attached to the bag by 0.5-in. outside diameter FEP Teflon tubes connected to the straight bore stopcock, and nitrogen was flushed through the bulbs for five minutes through the "T"-bore stopcock. The 100-mℓ syringe containing NO was attached to the "T" of the bulb connected to side 1 of the chamber. While briefly interupting the nitrogen flush, the NO was injected into the bulb. The nitrogen flush was resumed once the syringe was empty. Care was taken not to allow any oxygen to enter the bulb. NO_2 was injected into the bulb attached to side 2 of the chamber in an analogous manner. This same technique was also used to inject propene for propene-NO_x irradiations, n-butane and propene for tracer-NO_x-air or

CO-tracer-NO_x-air irradiations, and ethene, n-butane, isobutene and propene for surrogate irradiations performed during the first phase of the outdoor experiments. These compounds were usually injected into side 1 of the chamber. The bulb was then flushed for approximately five minutes.

Compounds that were liquids at room temperature and pressure, such as acetaldehyde, n-pentane, isooctane, toluene and m-xylene, were injected using a different technique. This method involved injecting the desired amounts of the liquids using a microsyringe into a 5-ℓ glass bulb equipped with a port for such injections. This glass bulb also had Teflon stopcocks at each end that were kept closed while the bulb was being dosed. Once the bulb was dosed, it was attached to side 2 of the chamber with a 0.5-in. outside diameter FEP Teflon tube and at the other end attached to a nitrogen source. The stopcocks were then opened, and the vaporized contents of the bulb were flushed into the chamber with nitrogen for ~20 minutes.

The above two techniques were employed for the surrogate components only during the first series of outdoor chamber experiments. For the second series of experiments, two cylinders of the surrogate hydrocarbon mixtures were purchased from Scott Environmental Technology, Inc. The first cylinder contained 105 ppm ethene, 77.3 ppm propene, 149 ppm isobutene and 165 ppm n-butane. The second cylinder contained 164 ppm n-pentane, 74.9 ppm toluene, 64.3 ppm m-xylene and 77.2 ppm isooctane. In both cylinders the balance was nitrogen. To introduce a total of ~4 ppmC hydrocarbon into the bag (the amount used in most of the surrogate runs), the contents of each cylinder were allowed to flow at 3 ℓ min^{-1} through the injection bulb for 12.5 minutes followed by a nitrogen flush for approximately five minutes. The components of the first cylinder were flushed through the same bulb that was used for the NO injection on side 1, and the components of the second cylinder were flushed through the same bulb that was used for the NO_2 injection on side 2.

For the ozone conditioning experiments, the ozone was prepared and injected as follows: A 5-ℓ bulb with vacuum Teflon stopcocks at each end was covered with black tape to avoid photolysis. A Welsbach ozone generator was used to produce a steady flow of ~1.3% O_3 in O_2. This O_3/O_2 mixture was used to flush the bulb for five minutes. The bulb was then attached to the outdoor chamber via a 0.5-in. FEP Teflon tube. The other end of the bulb was attached to a nitrogen supply. Both stopcocks were opened and the ozone was flushed into the chamber for five minutes.

In some experiments, additional injections of NO were made to one or both sides of the chamber on second or subsequent days of the run. These injections were generally carried out about one to two hours after the chamber was uncovered for that day. The injection procedure was as described above for the initial reactant injections.

The reactants were thoroughly mixed by manually agitating the sides of the chamber before dividing the chamber and before any sampling was begun. Following the division of the bag, any additional reactant injections to the individual sides were made, and samples were analyzed from both sides using all instruments. The bag was then uncovered to begin the irradiation; this generally occurred between 0900 and 1000 Pacific Standard Time (PST) for surrogate-NO_x-air runs, though for some characterization or conditioning runs of shorter duration the irradiations were begun later. For multi-day runs, the chamber was usually covered in the evening around 1500 PST and uncovered again around 0900 PST on the following day. This was carried out to avoid differential irradiation of the western side of the chamber (side 2) in the evenings and of the eastern side (side 1) in the early mornings. On the final day of the run, the run was terminated at 1500 PST or earlier depending on whether the reaction mixture was still exhibiting photochemical reativity (i.e., ozone formation).

Samples were taken for gas chromatographic analyses at at least hourly intervals during the daylight hours of the experiments, with samples alternating between each side of the chamber for dual chamber runs. Formaldehyde samples were also taken hourly, but in this case samples were usually taken simultaneously from each side of the chamber in dual chamber runs. No gas chromatographic or formaldehyde data were taken during nighttime hours. However, as indicated above, data from the continuous analyzers were automatically collected from each side of the chamber once an hour at nighttime and once every 30 minutes during daylight hours.

B. Indoor Chamber Experiments

1. Chamber

The ~6400-ℓ SAPRC indoor Teflon chamber employed in all the indoor chamber experiments for this program is shown schematically in Figure 4. The chamber consisted of a 2-mil thick FEP Teflon reaction bag which was constructed in a similar manner to the outdoor Teflon chambers, as described in Section II.A.1. The reaction bag was fitted inside an aluminum frame of dimensions of 8 ft x 8 ft x 4 ft. One edge was hinged to allow the bag to collapse to less than one-fifth of its maximum volume (see Figure 4).

The light source for this indoor Teflon chamber consisted of two diametrically opposed banks of 40 Sylvania 40-W BL blacklamps backed by arrays of Alzak-coated reflectors. The light intensity could be controlled by switching on or off sets of lights as previously described (Darnall et al. 1981), although for all the indoor runs reported here, the light intensity was held constant at 70% of its maximum. The intensity and spectral characteristics of this light source are discussed in Section III.B.1.

Pure, dry air for these experiments was provided by an air purification system which has been described in detail previously (Doyle et al. 1977). In this system, ambient air was drawn through Purafil beds (to remove NO_x), compressed by a liquid (water) ring compressor to 100 psig, and passed successively through a heatless dryer, a Hopcalite tower (to remove CO) and a second heatless dryer packed with activated coconut charcoal. The latter acts as a pressure-swing adsorption unit and routinely reduced the hydrocarbon levels (as measured in the chamber) to ~800 ppb methane, <5 ppb of C_2 hydrocarbons and propane and <1 ppb of all higher hydrocarbons.

2. Experimental Procedures

Before each experiment, the chamber was filled and emptied at least three times with purified air and then refilled. For the last fill, purified air humidified to ~50% relative humidity (RH) was employed. Prior to any reactant injections, background samples were analyzed using all of the gas chromatographic instruments to be employed during the run. NO, NO_2 and the various surrogate components were then injected individually. All gaseous reactants were injected using gas-tight,

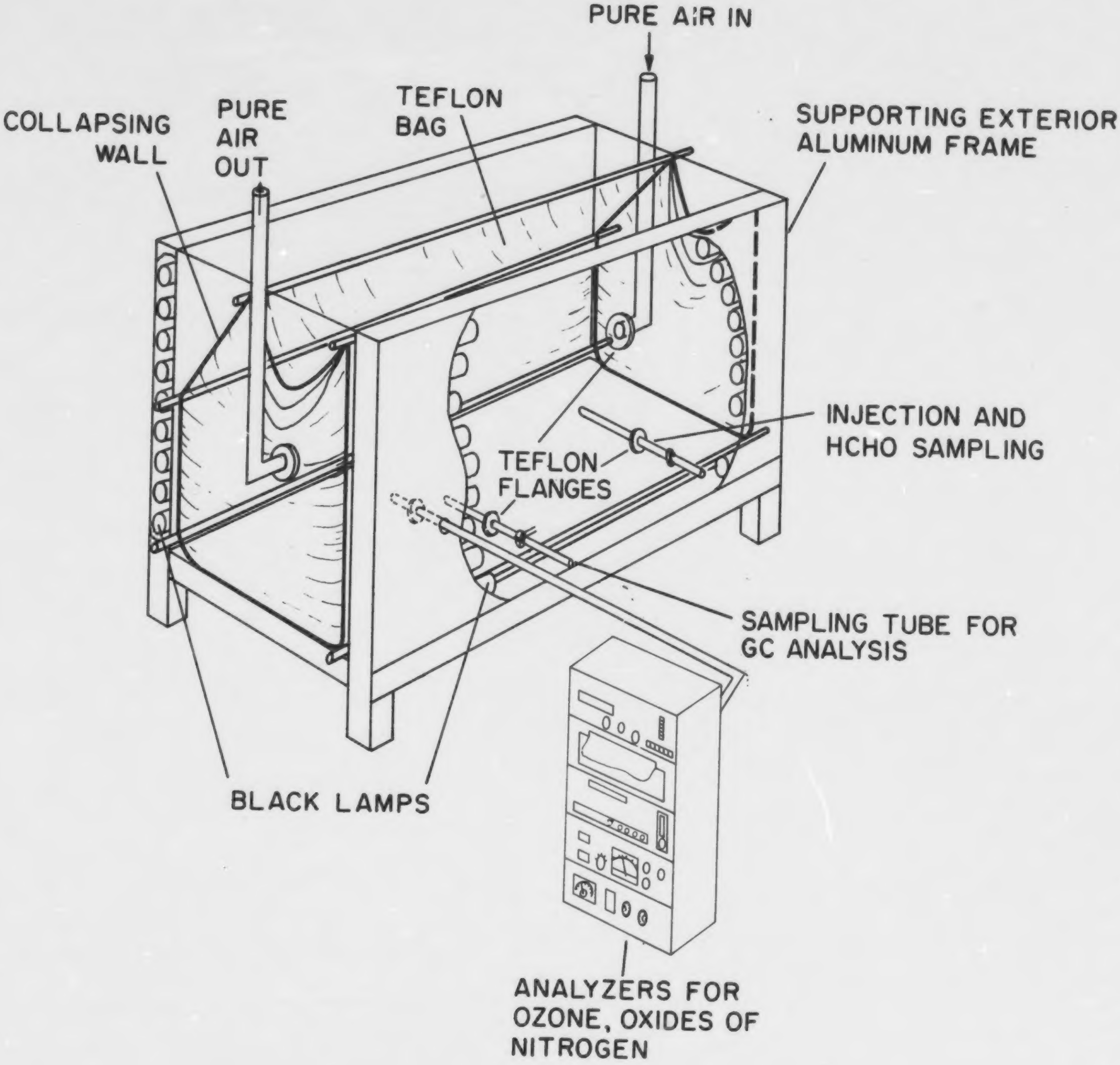

PURE AIR IN
COLLAPSING WALL
PURE AIR OUT
TEFLON BAG
SUPPORTING EXTERIOR ALUMINUM FRAME
INJECTION AND HCHO SAMPLING
TEFLON FLANGES
SAMPLING TUBE FOR GC ANALYSIS
BLACK LAMPS
ANALYZERS FOR OZONE, OXIDES OF NITROGEN

Figure 4. SAPRC all-Teflon indoor chamber with associated analytical instruments.

all-glass gas syringes and were flushed into the chamber by a stream of ultra-high purity N_2. For the liquid surrogate components, the desired amounts of the liquids were injected using a precision micropipette into a ~1-ℓ Pyrex bulb, whose contents were then evaporated and flushed into the chamber by a stream of ultra-high purity N_2. Gas chromatographic (GC) samples were then taken on all instruments prior to the beginning of the irradiations, which, as noted above, were all carried out at 70% of the maximum light intensity.

The procedures during the irradiation depended on the type of experiment being conducted. For the "multi-day" surrogate runs, the light intensity was held constant for 12 hours and the lamps were then turned off for 12 hours. GC and formaldehyde samples were taken hourly for at least the initial six hours of each simulated "day," and also immediately prior to turning off the lights. Data from the continuous monitoring instruments were collected every 15 minutes during the entire experiment using an Apple-computer-based data acquisition system similar to that employed in the outdoor experiments. In some experiments NO was injected into the chamber one hour after the resumption of the irradiation on the second or subsequent "days" of the irradiation. The procedures for the various conditioning, characterization and control runs were similar, except that they were generally carried out for shorter periods of time; the details are indicated on the data sheets in Volume II and the data sets in Volume III for the various types of runs.

C. Analytical Techniques

In this section, the analytical procedures employed for each set of compounds or physical parameters monitored in this program are described and their calibration technique and estimated accuracy and precision are discussed. Except as indicated, the same technique and calibration procedure for a given set of compounds or parameters was employed for both the indoor and outdoor chamber experiments.

1. Gas Chromatographic Analyses

Organic reactants and products were monitored using five different gas chromatographic systems, each suitable for a particular set of compounds. Samples for chromatographic analyses were withdrawn from the chamber using 100 mℓ gas-tight, all-glass syringes. The syringes were flushed at least three times with the sample gas before the sample for analysis was taken. A syringe was attached to the sample port of the chamber to withdraw a sample; in the case of the indoor chamber, the sample port was an ~18-in. x 1/4-in. Pyrex tube with a Becton-Dickinson stainless steel lever-lok stopcock manifold. The outdoor chamber had an ~18-in. x 1/4-in. FEP Teflon tube with a similar stopcock attached. Depending on the gas chromatographic analysis system, the contents of the syringe were either (1) flushed through ~2-mℓ stainless steel or ~10-mℓ heated glass loops and subsequently injected onto the column by turning a gas sample valve, or (2) condensed in a trap cooled with liquid argon, and then injected onto the column by simultaneously turning the gas sample valve and heating the loop with boiling water or ice water. The various gas chromatographic systems used, and the compounds they monitored, are briefly described below.

- Oxygenates such as acetaldehyde, acetone and 2-butanone, organic nitrates such as 2- and 3-pentyl nitrates and aromatic hydrocarbons such as toluene and m-xylene were monitored using the "C-600" gas chromatograph (GC). (Acetaldehyde could not be monitored in the first series of outdoor experiments because the column employed did not separate acetaldehyde and isooctane. For the second series of outdoor experiments, a new column allowing acetaldehyde to be monitored was used.) This system consisted of a Varian 1400 GC with a flame ionization detector (FID) and a 10-ft x 1/8-in. stainless steel column packed with 10% Carbowax 600 on C-22 Firebrick (30/60 mesh). The flow through this column was set at 50 mℓ min^{-1} and, as was the case with all of the GC's, the carrier gas was nitrogen. The hydrogen flow was kept at 45 mℓ min^{-1}, and the oxygen, used in the place of air to enhance sensitivity, was set at 250 mℓ min^{-1}. The detector was heated to 200 C, and the column was maintained at 75 C. 100-mℓ samples drawn from the chamber were trapped by pushing the gas sample through a 10-in. x 1/8-in. stainless steel tube packed with glass beads (80 mesh) and immersed in liquid argon. The sample was carried onto the column by then immersing the trap in boiling water and simultaneously actuating the gas sampling valve which was heated to 95 C to prevent adsorption of compounds.

- C_2-C_5 alkanes and alkenes were monitored using the "DMS" GC, which consisted of the electrometer and flame ionization detector from a Varian

1400 GC with a 34.5-ft x 1/8-in. stainless steel column packed with 10% 2,4-dimethylsulfolane on acid washed 60/80 mesh Firebrick. At the end of this column, before the detector, was a 2-ft x 1/8-in. stainless steel "soaker" column packed with 10% Carbowax 600 on Firebrick. The carrier nitrogen flow through these two columns was set at 50 mℓ min^{-1}, as was the hydrogen flow. The oxygen flow was 330 mℓ min^{-1}. The columns were maintained at 0 C and the detector was heated to 115 C. The 100-mℓ gas samples were trapped on a 10-in. x 1/8-in. stainless steel column packed with 10% 2,4-dimethylsulfolane on Firebrick, 60/80 mesh, immersed in liquid argon. The sample was then introduced to the column by simultaneously thawing the trap in ice water and turning the gas sampling valve.

- Methane, ethane, ethene and acetylene were monitored using the "PN" GC which consisted of a Varian 1400 GC with a flame ionization detector and a 5-ft x 1/8-in. stainless steel column packed with Porapak N, 80/100 mesh. The nitrogen carrier flow was set at 80 mℓ min^{-1}, the hydrogen at 60 mℓ min^{-1} and the oxygen at 400 mℓ min^{-1}. The column was maintained at 60 C, while the detector was heated to 130 C. When a sample was to be analyzed for methane, 100-mℓ of the sample was pushed through a 3-mℓ stainless steel loop. The sample in the loop was then transferred onto the column by actuating the gas sampling valve. Sampling for ethene, ethane and acetylene was accomplished by trapping the sample in a 11-in. x 1/8-in. stainless steel column packed with 10% Carbowax 400 on Firebrick, 30/60 mesh, immersed in liquid argon. The sample was thawed by immersing the trap in ice water and at the same time turning the valve so that the sample was transferred to the column.

- C_{5+} alkanes and alkenes, aromatic hydrocarbons and some oxygenates and alkyl nitrates were monitored by a Hewlett-Packard 5711A gas chromatograph with a flame ionization detector and a 30-m x 0.322-mm fused silica capillary column. This column, manufactured by J&W Scientific, Inc., had a film thickness of 1 μm composed of the bonded, liquid phase DB5. The nitrogen carrier flow was set at 0.6 mℓ min^{-1} and the makeup gas, also nitrogen, was set to 30 mℓ min^{-1}. The hydrogen and oxygen flows were maintained at 30 mℓ min^{-1} and 230 mℓ min^{-1}, respectively. Before a sample was taken, the column oven was cooled to -90 C. Sampling was accomplished by flushing 100 mℓ of sample through a dichlorodimethylsilane treated 10.2-mℓ glass loop. The GC gas-sampling valve, which was maintained at

145 C, was then actuated, and the sample was transferred onto the head of the column (at -90 C) over a period of 12 minutes. The column was then heated from -90 to -50 C over a 1.3-minute duration. The temperature program was then started with the column being heated from -50 to 200 C at a rate of 8 C min^{-1}.

- Peroxyacetyl nitrate (PAN) was monitored using a GC with an electron capture detector (ECD) which consisted of an Aerograph gas chromatograph with an ECD. The detector was equipped with a standing current control, and since the response was directly influenced by the standing current, it was maintained to within ±2% of a constant value during all experiments and calibrations. The GC used for the indoor experiments used a 12-in. x 1/8-in. FEP Teflon column containing 5% Carbowax 400 on Chromosorb G (80/100 mesh) operating at room temperature with a nitrogen carrier flow of 75 mℓ min^{-1}. That used for the outdoor experiments had a 14-in. x 1/8-in. FEP Teflon column packed with 5% Carbowax 400 on Chromosorb W (100/120 mesh) operating at room temperature with a nitrogen carrier flow of 36 mℓ min^{-1}. Analyses were carried out by flushing a ~2-mℓ loop with the sample, and then injecting the contents of the loop onto the column.

Calibrations of all GC's were performed at approximately two- to three-month intervals, and except for the ECD system used to monitor PAN, were accomplished in the same general manner. First, all gas flows were measured to verify that no changes had occurred that would indicate previous measurements were erroneous. After measuring these flow rates, a calibration mixture was made up using one of two methods. The calibration mixture, composed of known quantities of various compounds, was then injected into the proper GC. The elution time and height of each peak was recorded. The height of each peak was multiplied by the attenuation and the response in millivolts was obtained.

For gaseous compounds, two 2000-mℓ flasks, whose exact volumes had been determined by measuring with water, were flushed with nitrogen for 20 minutes, and then 2 mℓ of each pure gas was injected into the first flask with a 5-mℓ syringe. This flask was allowed to mix for 20 minutes, and then 2 mℓ from this flask was transferred into the second flask. The contents of this second flask were allowed to mix for 20 minutes. This resulted in a concentration of ~1 ppm of the gas in the second flask. Loop calibrations were performed by connecting this second flask directly to the loop and flushing the loop with the contents of the flask. Trap calibrations were accomplished by diluting a 5-mℓ sample from the second flask with nitrogen in a 100-mℓ syringe, and passing the contents of the syringe through the trap. For a flask containing 1 ppm of the compound, this was equivalent to sampling 100-mℓ of gas containing 50 ppb of the compound.

Calibration of compounds that were liquid in a pure state at room temperature was carried out using an all-glass carboy, of volume 49.95 ℓ, which was first cleaned by being heated from the inside with a heat gun, then flushed with the heat gun with the heat off until it reached room temperature, and finally flushed with nitrogen for one hour. The carboy was then dosed with 1 μℓ of each pure liquid to be calibrated using a 10-μℓ syringe. These were allowed to mix for one hour prior to any samples being taken. Trap and loop calibrations were both accomplished in the same way. A 1-mℓ sample was taken from the carboy with a 5-mℓ syringe and diluted with 99 mℓ of nitrogen. The samples were injected in the manner described previously. The exact concentration of each compound was calculated knowing the amount of liquid injected and its density.

Calibration samples of PAN were prepared in pressurized cylinders as described previously (Stephens et al. 1975), and the PAN concentration was determined by infrared absorption of the 8.6 μ band [absorption cross-section = 13.9×10^{-4} ppm^{-1} (Stephens and Price 1973)]. The contents of the cylinder were diluted using a flow manifold with calibrated rotometers to yield appropriate PAN concentrations in the range 5-50 ppb, and 100-mℓ samples were taken directly from the flow manifold using gas-tight, all-glass syringes.

The expected accuracy and precision of concentration measurements of most of the compounds determined by the above systems were, with the exception of PAN and acetaldehyde, ~5% or better. Due to varying peak widths, acetaldehyde concentrations were precise and accurate to ~20%. Peroxyacetyl nitrate measurements were estimated to have ~10% precision and ~25% accuracy.

2. Formaldehyde

Formaldehyde was monitored using the chromotropic acid technique. Samples for analysis by this technique were obtained by drawing, at 1 ℓ min^{-1}, 20 ℓ of air from the chamber through a single bubbler containing 10 mℓ of doubly distilled water. Samples taken from the outdoor chamber were taken through a 0.5-in. FEP Teflon probe, inserted into the chamber with the tip 18 inches from the chamber wall. The sample probe for the indoor chamber consisted of 0.5-in. Pyrex tube with the internal tip also located 18 inches from the chamber wall. A metal bellows pump at the downstream end of the bubbler with a calibrated flow meter and needle valve was used to pull the sample through the bubbler. The samples were developed by adding 0.10 mℓ of chromatropic acid (4,5-dihydroxy-2,7-napthalenedisulfonic acid disodium salt) to a 4.0 mℓ aliquot of the sample. The solution was acidified by diluting it to 10.0 mℓ with concentrated sulfuric acid. The chromatropic acid solution was prepared by dissolving 0.10 g of the salt in 10.0 mℓ of doubly distilled water. The developed solutions had a purple color and the absorbances were measured at 580 nm by a Beckman Model 35 spectrophotometer, after zeroing the instrument using a prepared blank. Instrumental drift was also periodically checked during the measurements using the same blank.

Periodic calibrations of the spectrophotometer and flow meters were carried out. The spectrophotometer was calibrated by subjecting a known concentration of formaldehyde salt to the same procedure as outlined above.

The accuracy and precision of this formaldehyde analysis technique depended upon a number of factors, including the calibration of the spectrometer and the efficiency of the bubbler in collecting formaldehyde from the air passing through it. In the past, the accuracy and precision of this technique had been quite variable, ranging from an optimum accuracy and precision of ~30%, to periods of anomalously low readings apparently due to problems with the bubbler, to periods of anomalously high and variable readings apparently due to contamination (see, for example, Pitts et al. 1979). Although attempts had been made to improve the reliability of this technique for routine use, they have only met with limited success.

Examination of the formaldehyde data gathered during the present experiments indicated that we still have significant problems with these measurements. In our outdoor chamber experiments, in both 1982 and 1983 highly variable results and large amount of scatter in the data were frequently observed. For example, pre-irradiation formaldehyde readings ranged from lows of ~0-10 ppb to ~150 ppb or higher, with no apparent pattern, with sometimes high and low readings obtained in pre-irradiation samples in the same runs. The formaldehyde data was even more scattered in the series of indoor surrogate-NO_x-air experiments, with no trends in the concentration data with time being discernible. On the other hand, much less scatter and more reasonable and consistent formaldehyde measurements were obtained in the latter outdoor experiments in both the 1982 and the 1983 series, and in the later series of indoor chamber experiments, though we have no explanation for this apparent improvement. Thus, for modeling purposes, we recommend that the formaldehyde data not be used in the indoor surrogate runs or in the outdoor runs where highly variable or anomalous values were obtained, and only with great caution in any case.

3. Continuous Monitoring Instruments

Ozone, nitrogen oxides, temperature and (for the outdoor runs only) the dew point depression were monitored continuously using the instruments described below. Except as noted, samples for analysis by these systems were taken from the gas sampling manifold described in Section II.A.1 for the outdoor chamber, or directly from a probe inserted ~18 inches into the chamber for the indoor chamber, using Teflon or glass sampling lines.

- Ozone was monitored using a REM Inc. Model 612 chemiluminescence ozone monitor for the outdoor chamber, and using a Dasibi Model 1003AH ozone monitor for the indoor chamber runs. Calibrations were carried out every two months against a Dasibi Model 1003AH ozone monitor transfer standard which in turn was routinely calibrated by the California Air Resources Board. The ozone source was a Monitor Labs Calibrator Model 8500, with four different ozone concentrations, and the dilution gas was Liquid Carbonic Company Medical Air. The analyzer being calibrated was first zeroed using Medical Air, then the calibrator was turned on to produce the highest concentration of ozone, ~0.3 ppm. Both analyzers were allowed to equilibrate before any readings were recorded, and the calibrated voltage on the REM was adjusted if any difference between the output of the two analyzers was recorded. The ozone concentration was then reduced, and the output from both instruments was observed to verify that the response was linear, this being repeated at two lower ozone concentrations. If the response was not linear, then corrective action was taken. Finally, the analyzer being calibrated was again zeroed with Medical Air. The precision and accuracy were both better than 5%.

- Nitric oxide and total oxides of nitrogen (NO_x + organic nitrates) were monitored using a Columbia Scientific Industries Series 1600 (for the outdoor chamber runs) or a Teco Model 14-B (for the indoor chamber runs) chemiluminescence oxides of nitrogen analyzer. Calibrations, using a Monitor Labs, Inc. Model 8500 calibrator as the dilution system, and a National Bureau of Standards cylinder of 97.4 ppm of NO in nitrogen, were performed bimonthly. The dilution gas was Liquid Carbonic Company Medical Air. The analyzer was first zeroed using Medical Air, then calibrated for NO by diluting NO in Medical Air and measuring the flow of each gas with a bubble flowmeter. The analyzer was allowed to equilibrate at each concentration for 30 minutes. The first concentration used was ~0.30 ppm. The potentiometers in the analyzer were adjusted, if necessary, to match the NO output of the analyzer with the actual concentration. Two more lower concentrations were used to verify linearity of the analyzer. The converter efficiency was checked by setting up a NO concentration of about 0.30 ppm, and then reacting this with a lesser concentration of ozone. If the converter was operating properly, the NO_2 would equal the difference in NO. The linearity of the converter was verified by using three different concentrations of ozone. After this procedure was completed, the analyzer was rezeroed with Medical Air. The accuracy and precision of this instrument in the absence of interfering nitrates (see below) was estimated to be comparable to those for the ozone monitors, i.e., better than 5%.

The analysis of NO_2 and NO_x was complicated by the fact that for such instruments the converters have been shown (Winer et al. 1974) to convert PAN, organic nitrates and HNO_3 to NO, and thus such species yield a positive interference in the NO_2 analysis cycle. (The NO data are unaffected.) Conversion of PAN and organic nitrates has been shown to be essentially quantitative (Winer et al. 1974) for the molybdenum converter employed in the Teco analyzer, but this has not been shown to be the case for the converter employed in the Columbia Scientific Industries instrument, and preliminary data from our laboratories have indicated that the conversion of PAN was not quantitative. It should be noted that organic nitrates are expected to be formed in significant yields from larger alkanes such as the isooctane present in the surrogate mixture, though the nitrates expected to be formed from those compounds could not be monitored due to lack of authentic samples for calibration purposes (since they are not available commercially). Therefore, no correction for this interference on the NO_2 data was attempted.

An additional complication in these analyses concerns the fact that HNO_3, a major NO_x sink in NO_x-organic-air irradiations, can also interfere with NO_2 readings. However, because of its tendency to be absorbed on the Teflon sampling lines this interference is non-quantitative (Pitts et al. 1981). This resulted on occasion in erratic NO_2 readings in the later periods of some multi-day indoor chamber runs, presumably due to HNO_3 saturating the Teflon sampling lines and being transported into the NO_2 converter. Less erratic (and lower) NO_2 readings were obtained when a nylon filter, which quantitatively removes HNO_3 (Joseph and Spicer 1978), was placed in line between the chamber and the NO_x analyzer. However, the nylon filter was not routinely employed in these experiments; when used, it is indicated on the data sheets.

- Temperature was monitored in the outdoor runs using a Doric Model DS 350-T3 digital thermocouple indicator, and in the indoor runs with an Analogic Model AN 2572 Digital thermocouple indicator, in both cases using iron-constantan thermocouples. For the outdoor runs, a thermocouple was installed in each manifold sample port so the air temperature was measured immediately as it flowed out of the chamber (see Section II). For the indoor chamber runs, the thermocouple was installed in a probe inserted into the center of the chamber. This instrument was calibrated periodically using ice water as the source for 0 C and boiling water as the source for 100 C. The accuracy was better than 5%, and the precision was better than 1%.

- The dew point depression was monitored in the outdoor runs only, using an EG&G International, Inc. Model 880 dew point hygrometer. This instrument was calibrated periodically against a sling psychrometer. This instrument required a daily to weekly cleaning and maintenance, and often time was not available in the schedule to perform these tasks. Thus the precision of the data from this instrument observed during many of the outdoor runs was not particularly good, and these measurements should probably be considered to be primarily qualitative in nature, and should be considered to be invalid in experiments where they are highly scattered.

4. Light Intensity

Light intensity was monitored continuously for the outdoor chamber runs by both a UV radiometer and by the quartz tube NO_2 photolysis rate measurement technique developed by Zafonte et al. (1977). For the indoor chamber runs, where the light intensity was constant, continuous light intensity measurements were not necessary. The light intensity was measured periodically using the quartz tube NO_2 photolysis rate technique. This technique and the UV radiometer measurements employed in the outdoor chamber runs are discussed below:

- UV radiation (λ = 290-390 nm) in the outdoor irradiations was monitored continuously using an Eppley radiometer located on the roof of the laboratory adjacent to the chamber. For the first series of outdoor experiments, data were recorded as six-minute averages during the time the chamber was uncovered. For the second series of runs, the data recorded on the strip charts was manually digitized in such a manner that the actual diurnal variations in the light intensity could be approximated by straight lines between the recorded points, and the data tabulations give both these detailed digitized data and 10-minute averages (calculated by the area under the detailed curves divided by the time interval) of these data. The precision of these UV measurements were found to be generally better than 5%. This instrument was calibrated at the factory both several years before and several months after the time these experiments were carried out, during which time the sensitivity of the instrument had decreased by 20%. The reported data employ the latter calibration. These data can also be placed on an absolute basis by comparison with the NO_2 photolysis rate measurements; this is discussed in Section III.B.7.

- A more absolute, though inherently less precise, measurement of light intensity in these experiments were the measurements of the NO_2 photolysis rates, k_1, which were carried out for both indoor and outdoor chamber runs.

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (1)$$

In both cases, the quartz tube technique of Zafonte et al. (1977) was employed. For the outdoor runs, the data were recorded every 10 minutes at the same time the data from the continuous analyzers were recorded; for the indoor chamber, a single average value was determined from separate actinometry experiments conducted approximately once a month.

In this technique, the reactor cell consisted of a 100-cm segment of 25-mm (nominal) quartz tubing with 1/4-in. outside diameter extensions at each end. The inside diameter of this tube was measured at both ends using calipers and had an average value of 21.44 mm. For the outdoor chamber, the first 20.5 cm of the tube were blackened to permit plug flow conditions to be established before photolysis occured. Likewise, the final 7.0 cm on the outlet side were blackened to terminate photolysis before sampling began. This left 72.5 cm over which photolysis was allowed to occur. The tube for the indoor chamber was not blackened at either end.

The NO for the actinometry experiments for the outdoor chamber was obtained from a Scott-Marrin, Inc. tank mixture of 100 ppm NO_2 in nitrogen. The mixture was further diluted with nitrogen using calibrated flow meters giving a final average concentration in the cell of 1-2 ppm. The nitrogen dioxide for the indoor chamber was obtained from a Scott-Marrin, Inc. tank mixture of 1.5 ppm NO_2 in nitrogen, and was not diluted further. The NO_2 flow entered the reactor cell via 1/4-in. blackened FEP Teflon tubing, attached with a 1/4-in. stainless steel Cajon ultra-torr union. The exhaust from the cell was connected to the sampling line of the NO_x analyzer, and the excess was vented to the atmosphere via a "T". These sample lines were also blackened FEP Teflon tubing, 1/8-in. for the outdoor chamber and 1/4-in. for the indoor chamber.

Under typical conditions, the gas flow was set to 37 $m\ell\ s^{-1}$. With an exposed cell volume of 262 $m\ell$, a NO_2 residence time of 9.1 sec was established within the cell. This allowed a sufficient buildup of NO which could then be accurately measured.

NO and NO_2 were measured using a chemiluminescence NO-NO_2-NO_x monitor (a Bendix Model 8101-B for the outdoor experiments, and a Teco Model 14-B for the indoor experiments). NO and NO_2 were alternately measured on a 30-sec cycle. The maximum sensitivity for both gases was 5 ppb. During photolysis, NO concentrations generally ranged from 100-150 ppb. Nitrogen dioxide was measured by chemiluminescence after initial reduction to NO.

Caution was exercised to ensure efficient operation of the reduction catalyst. The NO_x analyzer was calibrated bimonthly using the same procedure as for the NO_x analyzer (see above) sampling the contents of the chamber.

The precision of these NO_2 actinometry measurements was generally ~5-10%. This technique as used was inherently less precise and less capable of following rapid changes in light intensity than was the UV radiometric measurement technique. The accuracy of the NO_2 actinometry measurements were determined by a number of factors, including the accuracy of the NO_x analyzer, the extent to which plug flow conditions in the tube had been established, and whether the tube was placed in a location in which the light intensity and spectral distribution accurately reflected that in the chamber. In the latter regard, it should be noted that the quartz tube was located underneath one of the sides of the outdoor chamber and that the light had to pass through both layers of the Teflon bag surface before reaching the tube, which meant that the intensity of the light reaching the tube would be somewhat lower than the intensity of the light within the outdoor chamber. In addition, periodically the shadow from the outdoor chamber framework would fall on the tube, resulting in anomalously low light intensity readings. Thus in order to obtain both a sufficiently accurate and precise measurement of the variation of the light intensity during the course of these outdoor chamber experiments, both the UV radiometer and the NO_2 photolysis rate data must be employed. This is discussed further in Section III.A.7.

SECTION III

RESULTS AND DISCUSSION

A. Outdoor Chamber Studies

A total of 55 single and multi-day outdoor chamber experiments were carried out in the two years of this program, including 18 multi-day surrogate-NO_x-air irradiations, 6 propene-NO_x-air conditioning runs, 10 NO_x-air and/or CO-NO_x-air runs, 4 acetaldehyde-air irradiations, 20 side equivalency tests, 4 O_3 dark decay rate determinations and 2 pure air and/or CO-air irradiations (with several runs serving more than one purpose). As indicated in the Introduction, the outdoor chamber studies were carried out in two phases, the first, consisting primarily of side equivalency tests, during the autumn-winter of 1982, and the second during the summer and autumn of 1983. The second phase included the bulk of the multi-day surrogate runs. Table 2 gives a chronological listing of all of the outdoor runs carried out in this program, together with a brief summary of the description, purpose, experimental conditions and major results of each experiment.

Detailed tabulations of the data for the runs listed in Table 2 are given in Volume II of this report, and these data are given in computer readable format in Volume III. In addition to giving the relevant experimental measurements made during each run, the computer printouts and data sets given in Volumes II and III indicate which instrument was used for each set of measurements, and give overall averages for the major physical parameters measured during the runs. Comments taken from the laboratory notebooks describing the experimental operations, general weather conditions and any relevant observations, problems or special situations which occurred during the run are also included on these tabulations.

In the following sections, the results obtained in these experiments are summarized and discussed. The results of the various types of characterization runs are considered first, followed by a discussion of the light intensity measurements made during these outdoor experiments, and then the results of the multi-day surrogate runs are discussed. A detailed interpretation and modeling study of these experiments is outside the scope of this program, but the major experimental observations in these experiments are summarized, and data which need to be taken into

Table 2. Summary of Outdoor Chamber Experiments

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
				New Bag #26		
146	8/23/82	Acetaldehyde-air	Measure NO_x offgassing in new, unconditioned bag	Undivided bag CH_3CHO = 0.46 ppm 2-day irradiation Began at 0955 PST Not covered overnight	Cloudy weather	No PAN or O_3 formed; therefore NO_x offgassing minor in new bag
147	8/25/82	O_3 decay	Condition bag for O_3 Determine dark O_3 decay rate	Undivided bag O_3 = 5.6 ppm - dark	Dark run	The overall O_3 decay rate was 0.88% hour^{-1}, within the range previously observed for these bags
148	8/30/82	Propene-NO_x-air conditioning	Bag conditioning	Undivided bag Propene = 1.3 ppm NO = 0.32 ppm NO_2 = 0.08 ppm 1-day irradiation + 1 night Run started at 0907 PST Not covered overnight	Mostly clear weather	0.79 ppm O_3 formed, decreasing to 0.6 ppm overnight Final uncorrected NO_2 was 0.21 ppm, decreasing to 0.10 ppm overnight
149	9/1/82	Pure air vs. CO-air	Determine background reactivity of newly conditioned bag	Divided bag Side 1: ~40 ppm CO Side 2: No injections 1-day irradiation began at 1007 PST	Warm weather, high clouds	O_3 formation rates: CO side (side 1) 12 ppb hour^{-1} Pure air side (side 2) 9.6 ppb hour^{-1} These rates within expected range
150	9/2/82	NO_x-air vs. CO-NO_x-air	Determine chamber radical input rates for new bag using two techniques Further study background reactivity	Divided bag Initial NO = 0.28, NO_2 = 0.13, propene, n-butane tracers, both sides. 40 ppm CO added to side 1 1-day irradiation began at 0950 PST	Sunny and warm weather	Side 1 (CO) Side 2 -d[NO]/dt(ppb min^{-1}) 0.4 0.1 Radical source (ppb min^{-1}) ~0.3 ~0.06 Final O_3 (ppb) 44 0 Side 2 - radical source and NO oxidation rate within range observed for new bag Side 1 - radical source anomalously high

(continued)

Table 2 (continued) - 2

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
151	9/8/82	Surrogate vs. surrogate	Test for side equivalency Assess reactivity of SAI-recommended surrogate	Divided bag Injections made prior to bag division. 1.7 ppmC surrogate, 0.3 ppm NO_x 3-day irradiation started at 1037 PST Bag not covered overnight	Day 1: Cloudy, rained in evening Day 2: clear and warm Day 3: Cloudy	Day 1: No O_3 formation on either side NO conversion slightly faster on side 1 Day 2: Side 1: maximum O_3 = 0.11 ppm at 1335 PST Side 2: maximum O_3 = 0.31 at 1643 PST Day 3: Side 1: O_3 increased from ~0 to ~0.1 ppm Side 2: O_3 essentially constant at ~0.2 ppm Sides not equivalent: Side 1 more reactive on day 1, side 2 more reactive on day 2
152	9/20/82	NO_x-air	Test for side equivalency regarding radical input rates and reactive hydrocarbon contamination	Divided bag NO = 0.3 ppm, NO_2 = 0.08 ppm. Propene + n-butane tracers, each side. 4-hour irradiation began at 1013 PST	Sunny and warm weather	Side 1 Side 2 -d[NO]/dt (ppb min^{-1}) 0.2 0.2 Radical source (ppb min^{-1}) 0.18 0.13 Difference between sides not significant
153	9/21/82	Surrogate	Re-condition bag sides equally Data for surrogate run in undivided bag	Undivided bag Nominal 1.8 ppmC surrogate, 0.4 ppm NO_x 2-day irradiation began at 0930 PST Bag not covered overnight	Clear and warm weather both days	Day 1: maximum O_3 = 0.139 at 1456 O_3 and NO_2 reacted during the night Day 2: O_3 increased from ~0 to 0.2 ppm NO_2 (uncorrected) increased from nighttime low of 50 ppb to 69 ppb
154	9/23/82	NO_x-air attempt		Aborted due to injection error		
155	9/28/82	NO_x-air	Same as run OTC-152	Divided bag NO = 0.26 ppm; NO_2 = 0.09 ppm Propene + n-butane tracers, both sides 4-hour irradiation began at 1005 PST	Water found in bottom of bag before run; poured out Warm weather; scattered clouds	Side 1 Side 2 -d[NO]/dt (ppb min^{-1}) 0.12 0.51 Radical source (ppb min^{-1}) ~0.3 0.4 In contrast with run OTC-152, side 2 has significantly higher radical source and apparent contamination by reactive organics. Radical sources in both sides high even for an old bag. May be due to water in bag

(continued)

Table 2 (continued) - 3

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
156	9/29/82	Surrogate attempt		Aborted due to unfavorable weather		
157	9/30/82	Surrogate vs. surrogate	Test for side-equivalency on re-conditioned bag	Divided bag Nominal 3 ppmC surrogate, 0.4 ppm NO_x 2-day irradiation began at 0935 PST Bag not covered overnight	Clear, cool weather Side 1 leaked severely, completely deflated by day 2	Day 1: Side 1: O_3 maximum = 0.06 at 1348 PST Side 2: O_3 maximum = 0.34 at 1629 PST Day 2: Side 1: Deflated-data not reliable Side 2: Ozone declined NO_x readings constant Sides very inequivalent Bag obviously needed replacing
				New Bag #27		
158	10/4/82	O_3 decay	Condition bag for O_3 Determine dark O_3 decay rate	Undivided bag Initial O_3 = 4.55 ppm 2-day run, dark		Overall O_3 decay rate was ~1.1% hour^{-1}, which can be compared to the "typical" range of (0.3-1%) hour^{-1}
159	10/6/82	Propene vs propene	Condition bag Test for side equivalency	Divided bag Propene = 1.3 ppm, NO_x = 0.6 ppm both sides 1-day irradiation began at 0900 PST	Sunny and warm weather	Side 1: O_3 maximum = 0.83 ppm 1340-1440 PST Side 2: O_3 maximum = 0.88 ppm 1420-1450 PST O_3 formation and NO oxidation occurred at same rate on both sides. NO_2 declined after its maximum somewhat faster on side 1
160	10/7/82	NO_x-air	Test of radical input rates and reactive organic contamination for newly conditioned bag	Divided bag NO = 0.25, NO_2 = 0.08 ppm, propene + n-butane tracers, both sides 4-hour irradiation began at 1000 PST	Cool, hazy-sunny weather	Side 1 Side 2 -d[NO]/dt (ppb min^{-1}) 0.08 0.08 Radical source (ppb min^{-1}) 0.04 0.03 Within the range expected of newly conditioned bags. Clearly no side inequivalency
161	10/12/82	Pure air	Determine background reactivity of newly conditioned bag	Undivided bag No injections made Irradiations began at 0830 PST Bag not emptied after run	Clear, warm weather	33 ppb O_3 formed in 354 minutes O_3 formation rate = 4.7 ppb hour^{-1}, within the normal range

(continued)

Table 2 (continued) - 4

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
162	10/13/82	NO_x-air irradiation in previously irradiated pure air	Determine radical source and reactive organic contamination in newly conditioned bag. Determine whether using previously irradiated pure air affects reactivity	Divided bag Air from run OTC-161 used Bag covered between runs NO = 0.24 ppm, NO_2 = 0.10 ppm, propene, n-butane tracers in both sides >4-hour irradiation began at 1000 PST	Clear, warm weather	Side 1 Side 2 -d[NO]/dt (ppb min^{-1}) 0.06 0.08 Radical source (ppb min^{-1}) 0.03 0.03 Results essentially duplicate run OTC-160; using pre-irradiated pure air has no effect
163	10/14/82	Surrogate vs surrogate	Test side equivalency in newly conditioned bag	Divided bag Nominal 3 ppmC surrogate, 0.3 ppm NO_x 2-day irradiation began at 0900 PST Bag covered at 1530 PST Day 2: Bag uncovered at 0900 PST.	Day 1: Clear, warm weather Day 2: Cool weather, partly cloudy Bag removed after run	Day 1: Side 1: O_3 maximum = 0.158 ppm at 1520 PST Side 2: O_3 maximum = 0.326 ppm at 1530 PST Similar NO oxidation rate, both sides O_3 and NO_2 decreased overnight on both sides Day 2: O_3 increased on both sides with NO_2 (uncorrected) level at 50 ppb side 1, ~70 ppb side 2 Side 1: O_3 maximum = 0.159 at 1419 PST Side 2: O_3 maximum = 0.313 at 1459 PST Sides still very inequivalent in O_3 formation
164	10/18/82	N/A	Run for another program	N/A	Another bag used	N/A
165	10/20/82	Surrogate vs surrogate, sides reversed	Determine whether observed inequivalency of sides due to spatial orientation of bag	Divided bag Nominal 3 ppmC surrogate 0.3 ppm NO_x 1-day irradiation began at 1020 PST	Bag #27 replaced, but orientation changed 180°, and bag flipped top/bottom. Side 1 now has bag surface of old side 2 Cool, clear weather	Side 1: O_3 maximum = 0.102 ppm at 1500 PST Side 2: O_3 maximum = 0.213 ppm at 1510 PST Similar NO oxidation rates This run gives evidence that the inequivalency is due to orientation rather than bag surface contamination or conditioning

(continued)

Table 2 (continued) - 5

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
166	10/25/82	Surrogate vs surrogate-tarp background	Determine whether providing a more uniform background for bag would solve inequivalency problem	Divided bag Nominal 3 ppmC surrogate, 0.3 ppm NO_x 1-day irradiation began at 0950 PST	Three large canvas-like tarps were hung behind bag to provide more uniform reflection of sunlight into bag. Cool, partly cloudy weather	Side 1: essentially no O_3 formed NO_2 maximum = 0.263 ppm at end of day Initial NO consumption rate = 0.83 ppb min^{-1} Side 2: O_3 maximum = 84 ppb at end of day NO_2 maximum = 0.278 at 1258 PST Initial NO consumption rate = 1.14 ppb min^{-1} Side 2 still more reactive than side 1 Tarps did not solve problem
167	10/28/82	Surrogate vs surrogate-modified foreground	Determine whether providing a more uniform foreground for bag would solve inequivalency problem	Divided bag Nominal 3 ppmC surrogate 0.3 ppm NO_x 1-day irradiation began at 0914 PST	Tarps removed. Carpet underneath frame removed. Van moved in front of chamber to make reflected light from foreground appear to be more equal. Cold, partly cloudy weather	Side 1: Essentially no O_3 formed NO_2 maximum = 0.22 ppm at end of day Initial NO consumption rate = 0.79 ppb min^{-1} Side 2: Final O_3 = 163 ppb NO_2 maximum = 0.25 ppm at 1218 PST Initial NO consumption rate = 1.34 ppb min^{-1} Side 2 still more reactive than side 1; inequivalency greater than in previous run
168	10/29/82	NO_x-air	Recheck role of chamber effects regarding radical sources and reactive organics in observed side-inequivalency	Divided bag Initial NO = 0.24, NO_2 = 0.08 ppm, propene, n-butane tracers added both sides 3-hour irradiation, began at 1100 PST	Van removed and carpet replaced. Bag emptied but not flushed after previous runs Warm, partly cloudy weather	Side 1 Side 2 -d[NO]/dt (ppb min^{-1}) -0.01 0.10 Radical source (ppb min^{-1}) 0.03 0.06 Side 2 more reactive both in terms of radical source and NO oxidation rate, but neither measure outside of range observed in previous bags

(continued)

Table 2 (continued) - 6

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
169	11/3/82	Propene vs propene	Check side equivalency using a propene run to see if problem characteristic of surrogate employed	Divided bag Initial NO = 0.29, NO_2 = 0.26, propene = 0.64 ppm, both sides 1-day irradiation, began at 0907 PST	Cool, clear weather	Side 1: Essentially no O_3 formed NO_2 maximum = 0.39 ppm at end of day Initial NO consumption rate = 0.71 ppb min^{-1} Side 2: Final O_3 = 0.18 ppm NO_2 maximum - 0.44 ppm at 1228 PST Initial NO consumption rate = 1.4 ppb min^{-1} Side inequivalency clearly not due only to surrogate
170	11/4/82	Propene vs propene (rotated frame)	Test effect of bag orientation of side equivalency	Divided bag Bag filled 1/2 with pure air, 1/2 with clean, morning ambient air (pure air system malfunctioned) Initial NO ≡ 0.3, propene = 0.58 ppm Irradiation began at 1000 PST, aborted at 1108 PST	Bag frame turned Clockwise 90° Side 1, previously east side, now south side Bag half previously on side 1 still on side 1 Cool weather, scattered high clouds	Side 1: NO consumption rate ≡ 1.1 ppb min^{-1} Side 2: NO consumption rate ≡ 1.8 ppb min^{-1} Run aborted early because of rapid leakage of side 2 (~30% $hour^{-1}$) and obvious from first hour's data that sides are inequivalent
171	11/4/82	Propene vs propene (rotated frame)	Further test effect of bag orientation and bag surface on side equivalency	Divided bag Bag dumped from previous run (same day) and filled with unpolluted ambient air (pure air system down) Initial NO = 0.23, NO_2 = 0.27, propene = 0.53 ppm 1.5 hour irradiation began at 1438 PST	Frame orientation same as run OTC-170 Bag turned over so bag half on side 1 on run OTC-170 now on side 2 Clear, warm weather	Side 1: NO consumption rate = 0.69 ppb min^{-1} Side 2: NO consumption rate = 0.39 ppb min^{-1} Orientation which had faster side in run OTC-170 now has slower side - but same bag half. This looks like a contamination effect (but see results of runs OTC-163 and 165, which lead to the opposite conclusion)

(continued)

Table 2 (continued) - 7

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
172	11/11/82	Propene-NO_x-air conditioning	To condition the bag sides equally	Undivided bag Bag filled with unpolluted morning air (air system down) Initial NO = 0.33, NO_2 = 0.19, propene = 1.06 ppm 1-day irradiation began at 0911 PST	Cold, clear weather	Maximum O_3 = 0.36 ppm at 1346 PST, fell to 0.26 ppm by end of run
173	11/12/82	Propene vs propene	To determine whether conditioning by undivided propene-NO_x-air irradiation lessens side inequivalency	Divided bag Bag filled with unpolluted morning air (air system down) Initial NO = 0.33, NO_2 = 0.29, propene = 0.59 ppm, both sides 1-day irradiation began at 0905 PST	Same bag and frame orientation as run OTC-171 Cool, clear weather	Side 1: Maximum O_3 = 0.27 ppm at 1452 PST NO_2 maximum = 0.48 ppm at 1122 PST Initial NO oxidation rate = 2.9 ppb min^{-1} Side 2: Maximum O_3 = 0.14 at 1332 PST NO_2 maximum = 0.50 ppm at 1102 PST Initial NO oxidation = 2.8 ppb min^{-1} Conditioning caused sides to be roughly equivalent in NO oxidation rate, but much less O_3 is formed on side 2 (side 1 was the more "reactive" side in run OTC-171)
					Chamber relocated 20 feet to west. Frame rotated so side 1 to east again	
174	11/24/82	Propene-NO_x-air conditioning	To re-condition the bag sides equally to allow test of side equivalency in new location	Undivided bag Bag filled with unpolluted morning air Initial NO = 0.30, NO_2 = 0.30, propene = 1.15 ppm 1-day irradiation began at 0858 PST	Cool weather, partially cloudy, clouds increased throughout day	Maximum O_3 = 0.35 ppm at 1300 PST

(continued)

Table 2 (continued) - 8

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
175	12/2/82	Propene vs propene	Test side equivalency in new location using old, reconditioned bag	Divided bag Bag filled with unpolluted morning air Initial NO = 0.23, NO_2 = 0.30, propene = 0.59 ppm, both sides 1-day irradiation begun at 0936 PST	Cool, clear weather	Side 1: Final O_3 = 0.15 ppm Maximum NO_2 = 0.43 ppm at 1152 PST Initial NO oxidation rate = 2.0±0.15 ppb min^{-1} Side 2: Final O_3 = 0.11 ppm Maximum NO_2 = 0.42 ppm at 1132 PST Initial NO oxidation rate = 1.9±0.1 ppb min^{-1} Although side 2 formed somewhat less O_3, the sides are much closer to being equivalent than had been the case previously
				New Bag #28		
176	12/3/82	Ozone decay	Chamber conditioning determination of O_3 dark decay rate	Undivided bag Bag filled with unpolluted morning air 2.51 ppm O_3 injected Dark O_3 decay monitored for ~23 hours	Dark run	O_3 decay rate ≡ 0.5% $hour^{-1}$, which is in the range observed for previous bags
177	12/6/82	Propene-NO_x-air	Chamber conditioning	Undivided bag Bag filled with unpolluted morning air Initial NO = 0.31, NO_2 = 0.24, propene = 0.95 ppm 1-day irradiation began at 0936 PST	Cold, slightly hazy weather	Maximum O_3 = 0.57 ppm at 1438 PST Not all NO_x consumed
178	12/7/82	Propene vs propene	Test side equivalency for newly conditioned bag in new location	Divided bag Bag filled with unpolluted morning air Initial NO = 0.34, NO_2 = 0.36, propene = 0.72 ppm 1-day irradiation began 0916 PST	Cold weather Initially overcast, later hazy	Same results for both sides: No O_3 formed Maximum NO_2 = 0.57-0.58 ppm at end of day NO oxidation rate = 1.07 ppb min^{-1} Sides apparently equivalent with respect to NO oxidation rates

(continued)

Table 2 (continued) - 9

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
179	12/10/82	Propene vs propene	Further test side equivalency	Divided bag Bag filled with unpolluted morning air Initial NO = 0.32, NO_2 = 0.32, propene = 0.60 ppm 1-day irradiation began at 0946 PST	Clear, cold weather	Same results for both sides: Final O_3 ≅ 0.06 ppm, final NO_2 = 0.50 ppm, initial NO oxidation rate = 1.4 ppb min^{-1} Sides still equivalent
180	12/13/82	Surrogate vs surrogate attempt		Aborted due to unfavorable weather after the reactants were injected. Surrogate components injected as described below for run OTC-181.		
181	12/14/82	Surrogate vs surrogate	Test side equivalency using surrogate mixture Test side equivalency for multi-day run	Divided bag Bag filled with unpolluted morning air Nominal 3 ppmC surrogate, 0.4 ppm NO_x Half of surrogate injected on one side, half on other, but all injections made prior to bag division Bag uncovered at 0911 PST Bag covered at ~1600 PST Day 2: Bag uncovered at 0907 PST	Cool weather. Initially clear, some high clouds on day 1 and 2 Day 2: Side 2 deflated to ~20% its volume. Significantly higher surface/volume ratio than side 1.	Day 1: Same results both sides. Final O_3 = 0.07 ppm, NO_2 maximum = 0.35 around 1330 PST, initial NO oxidation rate = = 1.06 ppb min^{-1} Day 2, Side 1: Final O_3 = 0.24 ppm, NO_2 (uncorr) declined from 0.16 to 0.11 ppm. Side 2: Final O_3 = 0.18 ppm, NO_2 (uncorr) declined from 0.17 to 0.11 ppm Sides equivalent on day 1 - slightly less O_3 on side 2 on day 2 may be due to deflation of the bag on that side
182	12/16/82	Surrogate vs surrogate	Test side equivalency with surrogate mixture injected exactly as done for previous runs	Divided bag Bag filled with unpolluted morning air Surrogate liquids injected on side 2, gases on side 1 prior to bag division Nominal 3 ppmC surrogate, 0.4 ppm NO_x. 1-day irradiation began at 0859 PST	Cool weather, some scattered high clouds	Side 1: Final O_3 = 0.087, NO_2 maximum = 0.35 ppm around 1300 PST. Initial NO oxidation rate = 1.10 ppb min^{-1} Side 2: Same final O_3 and NO_2 maximum as side 1. Initial NO oxidation rate = 1.07 ppb min^{-1}. Sides still equivalent.

(continued)

Table 2 (continued) - 10

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
				Start of 1983 Series. New Bag No. 29		
183	6/22/83	Ozone decay	Condition bag for O_3 Determine O_3 dark decay rate	Undivided bag Initial O_3 = 1.26 ppm Monitored for >21 hours	Dark run	O_3 decay rate ~1-2%-hour^{-1}, roughly within the range previously observed; uncertain due to possible instrument malfunction
184	6/24/83	Aborted		Instrumentation problems		
185	6/27/83	NO_x-air	Determine background reactivity of new bag	Undivided bag Initial NO = 0.19 ppm NO_2 = 0.08 ppm Propene, n-butane tracers Uncovered at 1058 PST 2-hour run	Partly cloudy Hazy sunshine	-d[NO]/dt ≅ 0.02 ppb min^{-1} Radical input rate too low to measure ($\lesssim$0.03 ppb min^{-1})
186	6/29/83	Propene-NO_x-air	Bag conditioning	Undivided bag Initial NO = 0.27 ppm NO_2 = 0.29 ppm Propene = 1.26 ppm Uncovered at 0900 PST 6-hour run	Initially overcast Cleared 1200-1300 PST	Maximum O_3 = 0.82 ppm at 1410 PST
187	6/30/83	NO_x-air + CO-NO_x-air	Determine background reactivity of newly conditioned bag	Undivided bag Initial NO = 0.24 ppm NO_2 = 0.09 ppm Propene, n-butane tracers Uncovered at 1000 PST Unknown (due to error) amount of CO injected at 1200 PST. 4-hour run	Initially overcast Partly cloudy later	Before CO addition: -d[NO]/dt ≅ 0.05 ppb min^{-1} Radical input rate ≅ 0.02 ppb min^{-1} After CO addition: -d[NO]/dt ≅ 0.53 ± 0.02 ppb min^{-1} Radical input ran ≅ 0.04 ppb min^{-1}

(continued)

Table 2 (continued) - 11

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
188	7/5/83	NO_x-air + CO-NO_x-air	Repeat of run OTC-187	Undivided bag Initial NO = 0.25 ppm NO_2 = 0.10 ppm Propene, n-butane tracers Uncovered at 1015 PST 72.5 ppm CO added ~1220-1230 PST. 4-hour run	Hot, slightly hazy weather	Before CO addition: $-d[NO]/dt = 0.10 \pm 0.01$ ppm min^{-1} Radical input rate ≅ 0.02 ppb min^{-1} After CO addition: $-d[NO]/dt = 0.59 \pm 0.02$ ppb min^{-1} Radical input rate ≅ 0.04 ppb min^{-1}
189	7/7/83	Surrogate vs surrogate	Standard surrogate run and side equivalency test	Divided bag Initial NO = 0.35 ppm, NO_2 = 0.10 ppm, Surrogate = 3.98 ppmC, both sides Uncovered bag at 0915 PST Covered bag at 1515 PST Day 2: Side 2 had very low bag volume due to leakage Uncovered bag at 0900 PST Ended run at 1500 PST	Sunny and warm	Day 1: Max O_3 = 0.58 ppm, side 1 = 0.71 ppm, side 2 But initial NO consumption rate faster on side 1 Day 2: Side 1 Side 2 Initial O_3 (ppm) 0.27 0.45 Final O_3 (ppm) 0.35 0.35 Some side inequivalency observed, but much less than in 1982 series.
190	7/12/83	Surrogate vs surrogate	Side equivalency test with side reversed	Bag turned so side of bag previously on side 1 now on side 2 (Side No's refer to spatial orientation, not bag side) Divided bag Initial NO = 0.29 ppm, NO_2 = 0.13 ppm, Surrogate = 3.64 ppmC, both sides Uncovered bag at 0915 PST Covered bag at 1515 PST Day 2: Uncovered at 0900 PST Terminated run at 1500 PST	Clear, sunny hot weather	Side 1 Side 2 Day 1: Max O_3 (ppm) 0.70 0.67 Day 2: Initial O_3 (ppm) 0.46 0.42 Final O_3 (ppm) 0.34 0.35 Side 1 forms slightly more O_3 than side 2. The more reactive side has opposite orientation but same bag surface as more reactive side in previous run

(continued)

Table 2 (continued) - 12

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
191	7/15/83	Propene-NO_x-air	Condition bag sides equally	Undivided bag Initial NO = 0.26 ppm, NO_2 = 0.28 ppm, Propene = 1.21 ppm. Uncovered bag at 0900 PST 6-hour run	Sunny, hazy, warm weather	Final O_3 = 0.90 ppm
192	7/19/83	Surrogate vs surrogate	Side equivalency test	Divided bag Initial NO = 0.28 ppm, NO_2 = 0.19 ppm, Surrogate = 3.98 ppmC, both sides Uncovered bag at 0915 PST Covered bag at 1515 PST Day 2: Uncovered at 0900 PST ~0.14 ppm NO injected to Side 2 at 1032 PST Run terminated at 1510 PST	Clear, sunny, warm weather	Side 1 / Side 2 Day 1: Final O_3 (ppm) 0.74 / 0.75 Day 2: Initial O_3 (ppm) 0.41 / 0.48 Final O_3 (ppm) 0.28 / 0.64 (added NO side) Sides appear to be essentially equivalent
193	7/25/83	Aborted		Experimental problems		
194	7/27/83	Surrogate: variable HC	Effect of increasing initial surrogate in multi-day run	Divided bag — Side 1 / Side 2 Initial: NO (ppm) 0.24 NO_2 (ppm) 0.15 Surrogate (ppmC) 6.87 / 3.55 Bag uncovered 0940 PST Bag covered 1510 PST Day 2: Uncovered 0900 PST Run terminated at 1500 PST	Sunny, hazy, warm weather	Side 1 / Side 2 Day 1: Max O_3 (ppm) 0.74 / 0.60 Day 2: Initial O_3 (ppm) 0.46 / 0.41 Final O_3 (ppm) 0.37 / 0.47

(continued)

Table 2 (continued) - 13

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
195	8/2/83	Surrogate: variable HC	Effect of decreasing initial surrogate in multi-day run	Divided bag Side 1 Side 2 Initial: NO (ppm) 0.25 NO_2 (ppm) 0.16 Surrogate (ppmC) 1.83 4.04 Uncovered bag at 1020 PST Covered at 1518 PST Day 2: Uncovered at 0900 PST Covered at 1500 PST Day 3: Uncovered at 0900 PST Run terminated at 1244 PST	Day 1: Sunny and hot weather Day 2: Slightly hazy and hot Day 3: Hazy and hot	Side 1 Side 2 Day 1: Max O_3 (ppm) 0.16 0.68 Day 2: Initial O_3 (ppm) 0.01 0.43 Final O_3 (ppm) 0.40 0.42 Day 3: Initial O_3 (ppm) 0.21 0.36 Final O_3 (ppm) 0.20 0.32
196	8/10/83	Surrogate vs acetaldehyde	Measure NO_x offgassing rate for second day under same conditions of experimental run	Undivided bag initially Initial NO = 0.31 ppm NO_2 = 0.10 ppm Surrogate = 3.58 ppmC Uncovered at 1000 PST Covered at 1500 PST Day 2: Contents of bag pushed into side 2 and bag divided. Side 1 filled with pure air (not flushed) and ~0.4 ppm acetaldehyde added. Uncovered at 1015 PST Run ended at 1515 PST	Hazy and warm weather	Day 1: Max O_3 = 0.60 ppm Day 2: Initial O_3 = 0.32 ppm (side 2) Final O_3 = 0.37 ppm PAN formation rate ≡ 0.04 ppb min^{-1} (side 1)
197	8/24/83	Surrogate: variable NO_x	Effect of increasing initial NO_x in multi-day run	Divided bag Side 1 Side 2 Initial NO (ppm) 0.24 0.56 NO_2 (ppm) 0.14 0.22 Surrogate (ppmC) 3.59 (both) Uncovered at 1000 PST Covered at 1524 PST Day 2: Uncovered at 0900 PST Covered at 1525 PST Day 3: Uncovered at 0900 PST Run ended at 1100 PST	Hazy and warm weather	Side 1 Side 2 Day 1: Max O_3 (ppm) 0.62 0.15 Day 2: Initial O_3 (ppm) 0.40 0.01 Final O_3 (ppm) 0.40 0.65 Day 3: Initial O_3 (ppm) 0.30 0.44 Final O_3 (ppm) 0.23 0.40 Note that high NO_x side formed slightly more O_3 on day 2 than low NO_x side formed on day 1.

(continued)

Table 2 (continued) - 14

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
198	8/30/83	Surrogate: variable NO_x and HC	Effect of increasing both NO_x and surrogate levels in multi-day run	Divided bag Side 1 Side 2 Initial: NO (ppm) 0.45 0.13 NO_2 (ppm) 0.39 0.26 Surrogate (ppmC) 5.23* 3.48 *Note: due to injection error, amounts of liquid surrogate components have lower than normal amounts relative to other constituents. Also, NO apparently injected incorrectly, since initial NO_2/NO ratio is high. Bag uncovered at 1015 PST Covered around 1519 PST Day 2: Uncovered at 0855 PST Covered at 1519 PST Day 3: Uncovered at 0855 PST Run ended at ~1000 PST	Days 1-2: warm sunny, slightly hazy weather Day 3: warm and overcast	Side 1 Side 2 Day 1: Max O_3 (ppm) 0.70 0.67 Day 2: Initial O_3 (ppm) 0.32 0.48 Final O_3 (ppm) 0.52 0.40 Day 3: Initial O_3 (ppm) 0.39 0.34 Final O_3 (ppm) 0.35 0.30
199	9/7/83	Surrogate vs surrogate	Side equivalency test Effect of adding NO on day 2	Divided bag Initial NO (ppm) = 0.28, NO_2 (ppm) = 0.09, Surrogate (ppmC) = 3.51, both sides. Uncovered 0945 PST Covered 1550 PST Day 2: Uncovered 0900 PST 1000 PST: ~0.15 ppm NO added to side 2 Run terminated 1520 PST	Warm, sunny, hazy weather	Side 1 Side 2 Day 1: Max O_3 (ppm) 0.59 0.59 Day 2: Initial O_3 (ppm) 0.38 0.41 Final O_3 (ppm) 0.38 0.59 (added NO side) Side equivalency appears to be good

(continued)

Table 2 (continued) - 15

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
200	9/13/83	Acetaldehyde-air	Measure NO_x offgassing rates	Divided bag Initial $CH_3CHO \cong 0.5$ ppm, both sides Bag uncovered at 0930 PST Run terminated at 1500 PST	Warm, sunny, hazy weather	PAN formation rate $\cong$ 0.02 ppb min^{-1}, both sides
201	9/15/83	NO_x-air + CO-NO_x-air	Determine background reactivity of bag at two NO_x levels	Divided bag — Side 1 / Side 2 Initial: NO (ppm) 0.29 / 0.58 NO_2 (ppm) 0.09 / 0.18 Propene + n-butane tracers Bag uncovered at 0935 PST ~68 ppm CO (calculated) added to each side 1145-1200 PST. (Uncertainty in CO injection on side 2, may be less than amount calculated) Run terminated at 1500 PST	Sunny and warm weather	Side 1 / Side 2 Before CO addition: -d[NO]/dt (ppb min^{-1}) 0.27 / 0.12 Radical input rate (ppb min^{-1}) 0.12 / 0.11 After CO addition: -d[NO]/dt (ppb min^{-1}) 0.90 / 0.67 Radical input rate (ppb min^{-1}) 0.21 / 0.11
202	9/21/83	Surrogate: variable NO_x and HC	Repeat of run OTC-198	Divided bag — Side 1 / Side 2 Initial: NO (ppm) 0.62 / 0.31 NO_2 (ppm) 0.16 / 0.08 Surrogate (ppbC) 6.84 / 2.82 Uncovered at 1045 PST Covered at 1542 PST Day 2 Uncovered at 0900 PST Covered at 1530 PST Day 3 Uncovered at 0851 PST Run ended at 1220 PST	Days 1-2: mostly sunny and warm Day 3: overcast and warm	Side 1 / Side 2 Day 1: Final O_3 (ppm) 0.68 / 0.52 Day 2: Initial O_3 (ppm) 0.31 / 0.30 Final O_3 (ppm) 0.37 / 0.31 Day 3: Initial O_3 (ppm) 0.24 / 0.23 Final O_3 (ppm) 0.28 / 0.21

(continued)

Table 2 (continued) - 16

Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks
203	9/28/83	Surrogate: variable NO_x	Effect of varying initial NO_x in a multi-day run	Divided bag — Side 1 / Side 2 Initial: NO (ppm) 0.30 / 0.14 NO_2 (ppm) 0.09 / 0.04 Surrogate (ppmC) 3.48 Uncovered at 0954 PST Covered at 1520 PST Day 2: Aborted run due to rain	Day 1: Overcast with some sun Day 2: rain	Side 1 / Side 2 Day 1: Final O_3 (ppm) 0.23 / 0.39 Day 2: Initial O_3 (ppm) 0.05 / 0.30
204	10/4/83	Surrogate: variable NO_x	Repeat of run OTC-203	Divided bag — Side 1 / Side 2 Initial NO (ppm) 0.30 / 0.13 NO_2 (ppm) 0.09 / 0.05 Surrogate (ppmc) 3.44 Uncovered at 1000 PST Covered at 1530 PST Day 2: Uncovered at 1000 PST Covered at 1530 PST Day 3: Uncovered at 0900 PST ~0.13 ppm NO added to each side at 1000 PST Run ended at 1510 PST	Day 1: Warm and mostly sunny. Rained at night Day 2: Cool and hazy	Side 1 / Side 2 Day 1: Final O_3 (ppm) 0.30 / 0.38 Day 2: Initial O_3 (ppm) 0.12 / 0.27 Final O_3 (ppm) 0.20 / 0.25 Day 3: Initial O_3 (ppm) 0.11 / 0.18 Final O_3 (ppm)* 0.35 / 0.38 *After NO addition
205	10/10/83	Surrogate: variable NO_x	Effect of varying initial NO_x in a multi-day run. Compare results with high initial NO_x and no subsequent NO_x injections with low initial NO_x and subsequent NO_x injections	Divided bag — Side 1 / Side 2 Initial NO (ppm) 0.69 / 0.10 NO_2 (ppm) 0.15 / 0.04 Surrogate (ppmC) 3.59 Uncovered 1056 PST Covered at 1545 PST	Day 1: Cool and clear Day 2-3: Warm and clear Day 4: Warm and Hazy	Side 1 / Side 2 Day 1: Final O_3 (ppm) 0.04 / 0.39 Day 2: Initial O_3 (ppm) 0.01 / 0.28 Final O_3 (ppm) 0.46 / 0.51* Day 3: Initial O_3 (ppm) 0.21 / 0.36 Final O_3 (ppm) 0.32 / 0.44* Day 4: Initial O_3 (ppm) 0.21 / 0.31 Final O_3 (ppm) 0.11 / 0.28* *After NO addition

(continued)

Table 2 (continued) - 17

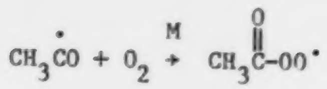
Outdoor Run No.	Date Started	Description	Purpose	Initial Concentrations and Experimental Operations	Experimental Conditions and Weather	Major Results and Remarks		
205 (continued)				Day 2: Uncovered at 0859 PST ~0.11 ppm NO added to side 2 at 1009 PST Covered at 1525 PST Day 3: Uncovered at 0900 PST ~0.11 ppm NO added to side 2 at 1009 PST Covered at 1530 PST Day 4: Uncovered at 0902 PST ~0.07 ppm NO added to side 2 at 1014 PST Run ended at 1400 PST Chamber was emptied but not flushed between runs OTC-205 and 206				
206	10/14/83	Acetaldehyde-air	Measure NO_x offgassing rate in a well-used bag	Divided bag Initial $CH_3CHO \cong 0.6$ ppm Bag uncovered at 0829 PST Run ended at 1440 PST	Mostly sunny and warm		Side 1	Side 2
						Final O_3 (ppm)	0.03	0.02
						Final PAN (ppb)	20	13
						PAN formation rate (ppb min^{-1})	0.06	0.04

account when the results of these runs are used for kinetic model testing are discussed.

1. Acetaldehyde-Air Irradiations

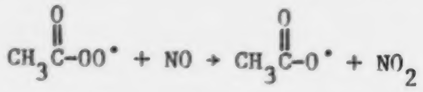
The purpose of acetaldehyde-air irradiations was to measure the rate of offgassing of NO_x (NO or NO_2) from the chamber walls upon irradiation. When irradiated in environmental chamber systems, acetaldehyde is consumed either by direct photoloysis or by reaction with OH radicals (which are always present during irradiations in environmental chambers), with the latter process giving rise to acetyl peroxy radicals.

$$CH_3CHO + OH \rightarrow CH_3\dot{C}O$$

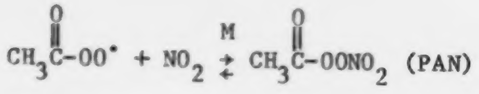


$$CH_3\dot{C}O + O_2 \xrightarrow{M} CH_3\overset{\overset{O}{\|}}{C}\text{-}OO^{\bullet}$$

If any NO_x is present in the system, even at sub-ppb levels, the primary fate of the acetyl peroxy radicals will be reaction with NO or NO_2, with the latter process giving rise to PAN, which is relatively stable in these systems, and whose formation can be readily monitored.



$$CH_3\overset{\overset{O}{\|}}{C}\text{-}OO^{\bullet} + NO \rightarrow CH_3\overset{\overset{O}{\|}}{C}\text{-}O^{\bullet} + NO_2$$



$$CH_3\overset{\overset{O}{\|}}{C}\text{-}OO^{\bullet} + NO_2 \overset{M}{\rightleftarrows} CH_3\overset{\overset{O}{\|}}{C}\text{-}OONO_2 \text{ (PAN)}$$

If measurable ozone is present in the system (as was the case for all of these irradiations except the first), then, since NO reacts rapidly with O_3 forming NO_2, $[NO_2]>>[NO]$ and thus PAN would be the dominant product. Of course, PAN formation can only occur if NO_x is present in the system. Furthermore, any NO_x offgassed from the walls would be converted to NO_2 (if emitted in the form of NO) by reaction with O_3 or acetyl peroxy radicals, with the NO_2 being converted to PAN by reaction with the excess acetyl peroxy radicals. Thus the PAN formation rate in acetaldehyde-air irradiations can be equated to the NO_x offgassing rate from the chamber walls.

A total of four acetaldehyde-air irradiations were carried out in the outdoor chamber during this program; one (run OTC-146) carried out using a new reaction bag, and the remainder after the bag had been used for a number of surrogate-NO_x-air or other types of NO_x-air irradiations. One of these (run OTC-196) was carried out on one side of the chamber immediately after the first day of a multi-day run, with the other side containing the second day surrogate mixture; two (runs OTC-196 and 206) were carried out with chamber not flushed between the preceding run (a surrogate-NO_x-air irradiation) and the acetaldehyde-air irradiation; and two (runs OTC-146 and 200) with the chamber flushed prior to the run, according to the normal procedure (see Section II.A.2). The results of these experiments are summarized in Table 3.

It can be seen from Table 3 that the NO_x offgassing rate, as measured by the PAN formation rate, ranged from approximately zero for a new, previously unused, chamber to ~0.04-0.06 ppb min^{-1} for irradiations following surrogate runs in which the chamber was not flushed. Based on the results of run OTC-200, flushing the chamber between runs appeared to decrease the NO_x offgassing rate by a factor of ~2, as might be reasonably expected. Since the usual procedure was to flush the chamber prior to an experiment, these data suggest that for the first day of a multi-day run, NO_x offgassing rates of 0.02-0.03 ppb min^{-1} might be representative, with rates of 0.04-0.06 ppb min^{-1} being more appropriate for subsequent days of multi-day runs.

It should be noted, however, that by necessity these runs measure the NO_x offgassing rates in the absence of excess NO_x in the system, so these measured NO_x offgassing rates might not be appropriate under conditions when excess NO_x is present. In particular, before the initially present NO_x has been consumed under these conditions, NO_x adsorption may be a more important process. However, the relatively low NO_x offgassing rates observed in these experiments suggest that when bulk NO_x is present, absorption/desorption processes are probably not important. NO_x offgassing may be more significant in affecting the results after the initial present NO_x has been consumed (the condition these acetaldehyde-air irradiations most closely represent).

Table 3. Results of the Acetaldehyde-Air Irradiations Carried Out in the Outdoor Chamber

OTC Run Number	146	196	200		206	
Chamber condition	New	Used - Not Flushed[a]	Used - Flushed[b]		Used - Not Flushed[c]	
Side	Undivided	1	1	2	1	2
Average						
T (C)	31±6	40±2	38±3		29±7	
UV ($mW\ cm^{-2}$)	1.7±1.2[d]	3.9±0.6	2.9±0.5		2.7±0.5	
k_1 (min^{-1})	-	0.31±0.04	0.22±0.04		0.22±0.04	
Initial CH_3CHO (ppm)	~0.05	~0.05	~0.05	~0.05	~0.06	~0.06
Irradiation time (hr)	28[e]	4.75	5.0	5.5	6.0	5.5
Final O_3 (ppb)	0	164	88	76	30	22
PAN (ppb)	0	13	8	6	20	13
PAN formation rate ($ppb\ min^{-1}$)	0	0.04	0.03	0.02	0.06	0.04

[a] Standard surrogate run carried out for one day in undivided chamber. On the second day, the contents of side 1 was pushed to side 2, the bag was divided, and side 1 was filled without flushing.

[b] Followed a two-day standard surrogate run with added NO on day 2 for side 2. Chamber flushed between runs.

[c] Followed a surrogate run (OTC-205) with variable NO_x with higher NO_x on side 1.

[d] Average for daylight period (0530-1850 PST) only.

[e] Two-day run. Chamber not covered overnight.

2. NO_x-Air and CO-NO_x-Air Irradiations

In order to obtain a measurement of the chamber radical source and of offgassing of reactive contaminants, a number of NO_x-air + CO-NO_x-air irradiations were carried out periodically throughout this program. These runs, the purpose of which has been discussed in detail elsewhere (Carter et al. 1982) consisted of irradiations of NO_x-air or CO-NO_x-air mixtures (with the NO_x levels representative of those employed in the surrogate-NO_x-air runs), with traces (~10 ppb) of propene and n-butane, for at least two hours. In the absence of chamber radical sources and reactive contaminants, this system is expected to be completely unreactive, and thus it is highly sensitive to these chamber effects.

Radical initiation rates were obtained by equating the initiation rates to termination rates due to the OH + NO_2 reaction [the major termination mechanism in this system (Carter et al. 1982)], with the rate of the latter being estimated from the known OH + NO_2 rate constant (Atkinson and Lloyd 1984) and the measured NO_2 and OH radical levels. The OH radical levels were monitored by measuring the relative rates of decay of the two organic tracers (propene and n-butane), which were consumed primarily by reaction with OH radicals:

$$\mathrm{OH + n\text{-}butane \rightarrow products} \tag{2}$$

$$\mathrm{OH + propene \rightarrow products} \tag{3}$$

However, propene was also consumed to some extent in this system by reaction with O_3 and $O(^3P)$ atoms,

$$\mathrm{O_3 + propene \rightarrow products} \tag{4}$$

$$\mathrm{O(^3P) + propene \rightarrow products} \tag{5}$$

and a correction for this must be made in the data analysis.

For propene and n-butane as the tracers, the relevant kinetic differential equations are:

$$\mathrm{dln[n\text{-}butane]/dt} = -k_2[\mathrm{OH}] \tag{I}$$

$$\mathrm{dln[propene]/dt} = -k_3[\mathrm{OH}] - k_4[\mathrm{O_3}] - k_5[\mathrm{O(^3P)}] \tag{II}$$

where k_2 and k_3 are the rate constants for the reaction of n-butane and propene with OH radicals, respectively, k_4 and k_5 are the rate constants for the reaction of propene with O_3 and $O(^3P)$ atoms, respectively, and the O_3 and $O(^3P)$ atom concentrations can be estimated based on the following assumptions: Since $O(^3P)$ is formed primarily from NO_2 photolysis and is consumed primarily by its rapid reaction with O_2, it can, to a very good approximation, be considered to be in photostationary state governed by these two reactions, and thus:

$$[O(^3P)] \cong \frac{k_1[NO_2]}{k_6[O_2][M]} \qquad \text{(III)}$$

where k_1 and k_6 are the rate constants for the photolysis of NO_2 and for the third-order reaction of $O(^3P)$ atoms with O_2 respectively:

$$NO_2 + h\nu \rightarrow NO + O(^3P) \qquad (1)$$

$$O(^3P) + O_2 + M \rightarrow O_3 + M \qquad (6)$$

Similarly, O_3 is also formed by NO_2 photolysis and, under the conditions of our experiments, was consumed primarily by its rapid reaction with NO. Thus it also can be assumed to be in photostationary state, and

$$[O_3] \cong \frac{k_1[NO_2]}{k_7[NO]} \qquad \text{(IV)}$$

where k_6 is the rate constant for the reaction O_3 with NO.

$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (7)$$

Equations (I) through (IV) can be combined and rearranged to yield

$$[OH] = (k_3-k_2)^{-1} \frac{d}{dt} (\ln \frac{[\text{n-butane}]}{[\text{propene}]}) - k_1 \; [NO_2](A + \frac{B}{[NO]}) \qquad \text{(V)}$$

where

$$A = \frac{k_5}{(k_3-k_2)k_6[O_2][M]}$$

and

$$B = \frac{k_4}{(k_3-k_2)k_7}$$

It can be seen from equation (V) that the correction for consumption of propene by reaction with O_3 and $O(^3P)$ atoms increases with $[NO_2]$ and $[NO_2]/[NO]$, respectively.

The radical flux, R_u, required to fit the data for a given run can be estimated from the fact that radical initiation and radical termination rates must balance. Since the only significant radical termination processes in this system are the reactions of OH radicals with NO and NO_2, and since HONO is in photoequilibrium after ~60 min of irradiation (Carter et al. 1982), then

$$R_u = k_8[OH]_{avg}[NO_2]_{avg} \tag{VI}$$

where k_8 is the rate constant for the reaction of OH radicals with NO_2,

$$OH + NO_2 \xrightarrow{M} HNO_3 \tag{8}$$

and $[OH]_{avg}$ and $[NO_2]_{avg}$ (the average OH radical and NO_2 concentrations for t >60 min) are experimentally determined. In general, in these irradiations the OH radical levels were approximately constant after the first hour of the irradiation.

It should be noted that equations (V) and (VI) are also valid for the conditions of the $CO-NO_x$-air irradiations, since the presence of CO introduces no new radical source or net radical sink. Thus, the reaction of CO with OH radicals

$$OH + CO \rightarrow CO_2 + H \tag{9}$$

does not represent a net radical sink since the H atoms formed react predominantly with O_2 to yield HO_2 radicals, which react with NO to regenerate OH radicals.

$$H + O_2 + M \rightarrow HO_2 + M$$

$$HO_2 + NO \rightarrow NO_2 + OH$$

However, these reactions do convert NO to NO_2. Thus if the NO_x concentrations are sufficiently low that the inorganic reactions involving NO to NO_2 interconversions [such as the thermal oxidation of NO, the $O(^3P) + NO_2$ reaction, and NO_3 radical chemistry (Atkinson and Lloyd 1984)] can be ignored, then in the absence of reactive contaminants which also convert

NO to NO_2, the rate of reaction 9 (R_9) can be approximated by the rate of NO consumption. This procedure allows an independent estimate of the OH radical levels.

$$\frac{d[NO]}{dt} \cong R_9 \cong k_9[OH]_{avg}[CO]_{avg}$$

$$[OH]_{avg} \cong \frac{-d[NO]/dt}{k_9[CO]_{avg}} \qquad \text{(VII)}$$

This technique for deriving the OH radical levels (and thus the radical source rate) is more uncertain than the tracer technique because of possible NO conversion by contaminants (see below). An approximate correction for this can be made if the CO-NO_x-air run was carried out in conjunction with a NO_x-air run (without added CO) by subtracting off the "background" NO oxidation rate observed in the absence of added CO, $-(d[NO]/dt)_o$ from that observed in the presence of added CO, $-(d[NO]/dt)_{CO}$. Thus

$$[OH]_{avg} \cong \frac{-(d[NO]/dt)_{CO} + (d[NO]/dt)_o}{k_9[CO]_{avg}} \qquad \text{(VIII)}$$

However, the tracer technique [utilizing equation (V)] is considered to be more accurate and precise for estimating OH radical levels; the primary utility of the added CO technique has been for assuring the validity of the tracer measurements (Carter et al. 1982).

In the absence of added CO, the NO oxidation rate will reflect the extent of offgassing of reactive contaminants, since these can cause NO oxidation via the following reactions.

$$\text{wall} \rightarrow \text{organic}$$

$$\text{organic} + OH \xrightarrow{O_2} RO_2$$

$$RO_2 \xrightarrow[\downarrow NO_2]{NO \downarrow} \text{products} + OH$$

If no such contamination existed, then the NO oxidation rate would be small, being primarily due to reactions of the propene tracer and the CO present in the matrix air, or the inorganic NO-NO_2 interconversion reactions (Carter et al. 1982). The NO_x-air runs without added CO are thus also useful in giving a qualitative measurement of the extent of such contamination.

The results of the NO_x-air and CO-NO_x-air irradiations carried out during the first phase of the outdoor chamber experiments are shown in Table 4, while those from the second phase are given in Table 5. The radical input rates and NO oxidation rates in the NO_x-air irradiations were within the range generally observed in these reactors (Carter et al. 1981, 1982, Pitts et al. 1983), and were relatively small, indicating that chamber effects related to unknown radical sources and offgassing or reactive contaminants were not a serious problem in most of these experiments. The results of most of the CO-NO_x-air irradiations (except for several anomalous runs, discussed below) were reasonably consistent with the associated NO_x-air irradiations, with the presence of CO having no significant effect on the radical levels as measured by the tracers, and with the radical levels measured by the NO oxidation rate (equation VIII) agreeing within their combined uncertainties with those measured by the tracer technique.

The most anomalous NO_x-air and CO-NO_x-air runs were runs OTC-150, 152 and 155, which were all carried out using bag #26, the first reactor employed in this program and one which was plagued with side inequivalency problems (see Section III.A.6). Run OTC-150 consisted of a NO_x-air irradiation on one side and a CO-NO_x-air on the other, with the OH radical concentration as measured by the tracer technique, and thus the radical input rate, being anomalously high on the CO-containing side. However, the radical levels as measured by the NO oxidation rate were more reasonable, suggesting the problem was with the tracer data for that run. On the other hand, the radical levels measured in runs OTC-152 and 155 were anomalously high on both sides of the reactor, indicating that bag #26 was probably contaminated. Thus, experiments carried out using that bag (which were primarily side equivalency tests) should probably not be used for model testing purposes.

Table 4. Results of the NO_x-Air Irradiations Carried Out in the Outdoor Chamber During the Fall-Winter of 1982

OTC Run No.	150		152		155		160		162		168	
Conditions[a]	New				SC, W		New, H		IA		SC	
Average[b]												
T (C)	46±2		36±3		25±2		26±1		36±3		28±2	
UV (mW cm^{-2})	3.8±0.2		3.8±0.3		4.3±0.5		3.6±0.4		4.1±0.2		2.6±0.7	
k_1 (min^{-1})	(~0.3)[c]		(~0.3)[c]		(~0.3)[d]		(~0.3)[d]		(~0.3)[c]		(~0.2)[d]	
Side	1	2	1	2	1	2	1	2	1	2	1	2
Average												
NO (ppm)	0.08	0.24	0.27	0.27	0.26	0.20	0.24	0.24	0.23	0.23	0.24	0.23
NO_2 (ppm)	0.29	0.14	0.08	0.09	0.05	0.09	0.08	0.09	0.10	0.10	0.08	0.09
CO (ppm)	40	3	-	-	-	-	-	-	-	-	-	-
Calculated												
-d[NO]/dt (ppb min^{-1})	0.41[e]	0.10	0.20	0.17	0.12	0.51	0.08	0.08	0.06	0.08	-0.01	0.10
[OH] (10^6 cm^{-3})[f]	~1.7 (0.6)	0.6	3.4	2.2	5.3	6.6	0.7	0.6	0.5	0.5	0.7	1.0
Radical input (ppb min^{-1})	~0.3	0.06	0.18	0.13	0.29	0.39	0.04	0.03	0.03	0.03	0.03	0.06

---

[a] Codes for conditions (unless otherwise indicated, used bag and clear weather). New - Bag not previously used for surrogate-NO_x-air runs. SC - scattered clouds. H - hazy sunshine. IA - previously irradiated pure air used. W - liquid water in bag at start of run.

[b] First hour of run not counted in average (see text).

[c] Estimated to be ~80% theoretical maximum (clear day).

[d] Estimates based on 80% theoretical maximum and UV radiometer readings, compared to values for a clear day.

[e] ~40 ppb O_3 formed in run. Value given is -d[NO]/dt + d[O_3]/dt.

[f] Value in parentheses for run OTC-150 calculated using the NO oxidation rate [equation (III)]. All other values calculated using the tracer technique [equation (V)], and were used to derive the radical input rate [equation (VI)].

Table 5. Results of the NO_x-Air Irradiations Carried Out in the Outdoor Chamber During the Summer-Fall of 1983

OTC Run No.	185	187A[a]	187B[a]	188A[a]	188B[a]	201A[a]		201B[a]	
Conditions[b]	New	OV-PC	OV-PC	H	H				
Average[c]									
T (C)	25±1	24±3	31±2	33±5	36±2	33±2		39±2	
UV (mW cm^{-2})	2.1±0.6	2.5±0.5	3.8±0.5	4.1±0.8	3.4±0.4	3.6±0.1		3.3±0.4	
k_1 (min^{-1})	-	0.21±0.04	0.33±0.05	0.34±0.01	0.30±0.03	0.25±0.03		0.25±0.03	
Side	Undiv.	Undiv.	Undiv.	Undiv.	Undiv.	1	2	1	2
Average									
NO (ppm)	0.19	0.24	0.20	0.24	0.18	0.27	0.58	0.15	0.49
NO_2 (ppm)	0.08	0.10	0.13	0.10	0.15	0.10	0.18	0.22	0.25
CO (ppm)	-	-	d	-	73[e]	-	-	68[e]	68[e]
Calculated									
-d[NO]/dt (ppb min^{-1})	0.06	0.05	0.53	0.10	0.59	0.27	0.12	0.90	0.67
[OH] (10^6 cm^{-3})[f]	<0.2	0.3	0.5	0.3	0.5 (0.5)	1.7	0.9	1.4 (0.7)	0.6 (0.6)
Radical input (ppb min^{-1})	<0.01	0.02	0.04	0.02	0.04	0.12	0.11	0.21	0.11

---

[a] Two-part run. "A" refers to first part, without added CO; "B" refers to second part with added CO.

[b] Codes for conditions (unless otherwise indicated, used bag and clear weather). New - bag not previously used for surrogate-NO_x-air runs. H - hazy sunshine. OV-PC - initially overcast; partially cloudy later.

[c] First hour of run not counted in average (see text).

[d] Intended amount injected ~50 ppm; actual amount uncertain due to injection error.

[e] Calculated based on amount estimated.

[f] Values in parentheses calculated using the NO oxidation rate [equation (VIII)]. All other values calculated using the tracer technique, and were used to derive the radical input rates [equation (VI)].

The only other instance where relatively high radical levels and NO oxidation rates were observed was run OTC-201 on side 1, where they were approximately twice those observed on the other side. However, a side equivalency test carried out two runs previously in the same bag (run OTC-199) indicated good side equivalency.

3. Pure Air and CO-Air Irradiations

Two pure air and CO-air irradiations were carried out in this program, both during the first phase. The first was run OTC-149, where ~40 ppm of CO was injected into one side and no injections were made into the other side. Ozone was formed on both sides, at a rate of 12 ppb hr^{-1} on the CO side and ~10 ppb hr^{-1} on the pure air side. Although, as discussed above, the results of the NO_x-air irradiations indicated that the bag employed in this run (bag #26) may have been contaminated, these rates were within the normal range previously observed [though somewhat higher than average (Carter et al. 1981)]. As one might expect, the presence of CO had no significant effect on the O_3 formation rate in the absence of injected NO_x.

The other pure air irradiation, run OTC-161, was carried out in bag #27 with the chamber undivided. The ozone formation rate in this run was ~5 ppb hr^{-1}, within the normal range previously observed (Carter et al. 1981).

4. Ozone Dark Decay Determinations

In order to characterize the rates of ozone destruction on the walls of these reactions, four dark O_3 decay determinations were carried out at various times during the course of this program, and the results are summarized in Table 6. All runs were carried out with the chamber in undivided mode; and, as indicated in the table, three of the four were carried out when the bag was new. The O_3 decay rates ranged from 0.5-1% hr^{-1}, and do not appear to depend significantly on whether the bag was new or used. These rates were within the range observed previously in previous outdoor chambers (Carter et al. 1981).

5. Propene-NO_x-Air Irradiations

The results of the one-day propene-NO_x-air irradiations which were carried out during both phases of the outdoor program are summarized in Tables 7 and 8. Two types of propene-NO_x-air irradiations were carried out: (1) Irradiations in the undivided bag carried out primarily for

Table 6. Results of the Ozone Dark Decay Measurements Carried Out in the Outdoor Chamber

OTC Run No.	147	158	176	183
Chamber condition	New	Used	New[a]	New
Average T (C)	28±6	20±7	11±5	26±6
Initial O_3 (ppm)	5.68	4.55	2.51	1.27[b]
Duration (hr)	27	22	25	14
O_3 Decay Rate ($\%\ hr^{-1}$)	0.9	1.1	0.5	~1-2[b]

[a] Unpolluted morning air used because of pure air system malfunction.
[b] Uncertain due to possible instrument malfunction.

chamber conditioning, either to condition new bags, or to re-condition used bags which had exhibited side inequivalency, or (2) divided chamber irradiations carried out for the purpose of testing side equivalency, as discussed in the following section. These propene-NO_x-air irradiations also serve as control runs for model testing purposes, since the chemistry of propene-NO_x-air irradiations is simpler and better characterized than that of multi-component surrogate-NO_x-air systems (Atkinson and Lloyd 1984), and extensive data exists from other environmental chambers concerning irradiated propene-NO_x-air systems.

6. Side Equivalency Tests

Since many of the experiments carried out in this program consisted of comparing the results of simultaneous irradiations of different mixtures in different sides of the divided chamber, it was important to establish that the two chamber sides were indeed "equivalent" - that is, would give the same result when the same mixture was irradiated under the same conditions. Thus, a series of side equivalency tests were carried out in which the same propene-NO_x-air or surrogate-NO_x-air mixture was irradiated on each side of the divided chamber. The results of these experiments, which differed considerably in the two phases of the outdoor program, are summarized in Table 2 and in the data tabulations in Sections III.A.5 (for the propene vs propene tests) or III.A.8 (for the surrogate vs surrogate runs), and are discussed in this section.

Table 7. Results of Propene-NO_x-Air Irradiations in the Outdoor Chamber: Runs OTC-148 through 173

OTC Run Number	148	159		169		170		171		172	173	
Conditions[a]	New					A,B		B,C		B	B,C	
Side	Undiv.	1	2	1	2	1	2	1	2	Undiv.	1	2
Initial												
NO (ppm)	0.32	0.26		0.28		0.30		0.23		0.33	0.33	
NO_2 (ppm)	0.24	0.32		0.26		0.28		0.27		0.19	0.28	
Propene (ppm)	1.32	1.27		0.64		0.57		0.54		1.06	0.59	
Time uncovered (PST)	0907	0900		0907		1000		1438		0911	0905	
Final												
O_3 (ppm)	0.79	0.83	0.88	0.02	0.18	0.01	0.01	0.01	0.01	0.26	0.25	0.09
NO_x + nitrates (ppm)	0.20	0.27	0.30	0.45	0.37	0.57	0.55	0.50	0.50	0.21	0.27	0.32
PAN (ppb)	0.21	0.46	0.50	0.01	0.11	-	-	-	-	0.38	0.25	0.15
HCHO (ppm)	0.43	0.41	0.49	0[c]	0.26	-	-	-	-	-	~0c	0.11c
Time covered/terminated (PST)	-[b]	1527		1500		1130		1608		1600	1602	
Average												
k_1 (min^{-1})	-	-		-		-		-		0.16±0.04	0.16±0.08	
UV ($mW\ cm^{-2}$)	3.8±0.6	3.4±0.7		-		-		-		1.9±0.7	-	
T (C)	40±4	33±4		25±3		27±1		31±2		24±7	26±3	

[a] Special condition codes (if no notation, chamber in standard orientation and position for 1982 series) [see Figure 2].

New - New bag, not previously employed for hydrocarbon-NO_x-air irradiations.

A - Bag frame turned clockwise 90°. Side 1 now north side. Bag in same orientation relative to frame.

B - Chamber filled (entirely or in part) with relatively unpolluted morning air, due to pure air system malfunction.

C - Bag orientation changed 180° relative to frame, and turned over. Bag side which was on north (side 1) during run OTC-170 now on south side (side 2).

[b] Bag not covered overnight. Averages given for 0907-1500 PST.

[c] Data highly scattered. Probably not reliable.

Table 8. Results of Propene-NO_x-Air Irradiations in the Outdoor Chamber: Runs OTC-174 through 191

OTC Run Number	174	175		177	178		179		186	191
Conditions[a]	A,B	A,B		New,A,B	A,B		A,B		New,C	C
Side	Undiv.			Undiv.	1	2	1	2	Undiv.	Undiv.
Initial										
NO (ppm)	0.30	0.23		0.30	0.34		0.32		0.27	0.26
NO_2 (ppm)	0.30	0.30		0.23	0.36		0.32		0.29	0.28
Propene (ppm)	1.13	0.59		0.95	0.71		0.59		1.26	1.21
Time uncovered (PST)	0900	0936		0936	0916		0946		0900	0900
Final										
O_3 (ppm)	0.30	0.15	0.11	0.57	~0	~0	0.06	0.05	0.81	0.90
NO_x + nitrates (ppm)	0.25	0.33	0.32	0.33	0.62	0.63	0.50	0.49	0.35	0.29
PAN (ppb)	-	-	-	-	-	-	-	-	0.26	0.10
HCHO (ppm)	-	0.33	0.26	0.49	0.18	0.19	0.21	0.21	-	0.33
Time covered/terminated	1500	1502		1518	1600		1555		1500	1500
Average										
k_1 (min^{-1})	-	0.13±0.05		0.22±0.09	0.10±0.06		0.17±0.07		-	0.31±0.04
UV ($mW\ cm^{-2}$)	-	1.9±0.4		-	-		-		2.6±1.5	4.2±0.5
T (C)	21±3	17±3		23±4	14±2		18±3		25±5	35±7

[a] Special condition codes (if no notation, chamber in standard orientation and position for 1982 series) [see Figure 2].

New - New bag, not previously employed for hydrocarbon-NO_x-air irradiations.

A - Chamber filled (entirely or in part) with relatively unpolluted morning air, due to pure air system malfunction.

B - Chamber relocated 20 feet to the west relative to its position in run OTC-173 and those previous. Also, frame oriented so side 1 to east, as prior to run OTC-170.

C - Chamber in standard orientation and position for 1983 series (see Figure 3).

As indicated previously, during the first phase of the outdoor program, the results of the side equivalency tests showed we had serious problems in this regard, and much of the work carried out during that phase of the program was aimed at elucidating and solving this problem. This problem of side inequivalency was most evident when bags #26 and #27 were employed (the first two used in the outdoor program). As discussed below, this effect seemed to resolve itself when the chamber was moved, the surrogate injection procedure was changed, and bag #27 was replaced. The magnitude of the inequivalency during this early period is shown in Figures 5 and 6, which show concentration-time profiles for selected species for a representative surrogate vs surrogate run (OTC-163) and a representative propene vs propene run (OTC-169), respectively.

In order to examine possible causes of the side-inequivalency observed when bags #26 and #27 were employed, Table 9 gives a concise summary of the history, conditions, and qualitative results of the various tests conducted, indicating in particular the orientation and bag surface on each side, and any changes which may have affected side differences. It can be seen that, except for the initial anomalous CO-NO_x-air run OTC-150, side 2 was consistently the more reactive side for bag #26, and for bag #27 up until run OTC-170. Indeed, side 2 remained the most reactive even after the bag was reoriented within the frame prior to run OTC-165, with the bag surface which had been the more reactive becoming the less reactive once it was oriented on side 1. This suggested the inequivalency may have been due to differences in lighting rather than contamination effects, but attempts to make the foreground or background environment around the chamber more uniform for runs OTC-166 and 167 had no significant effect. In addition, for run OTC-170 and those following, the orientation of the frame, and the bag within the frame, was changed several times as shown in Table 9, but in all cases, it was the same bag surface (designated "A" in the table) which had the higher reactivity, even when its orientation was changed 180^o. This suggests contamination effects, but the results of run OTC-163, where the opposite surface was the more reactive, indicate that this cannot be the only factor.

The side inequivalency problem became much smaller when the chamber (with bag #27) was relocated 20 feet to the west (see Figures 2 and 3 in Section II.A.1), and essentially disappeared when bag #27 was replaced

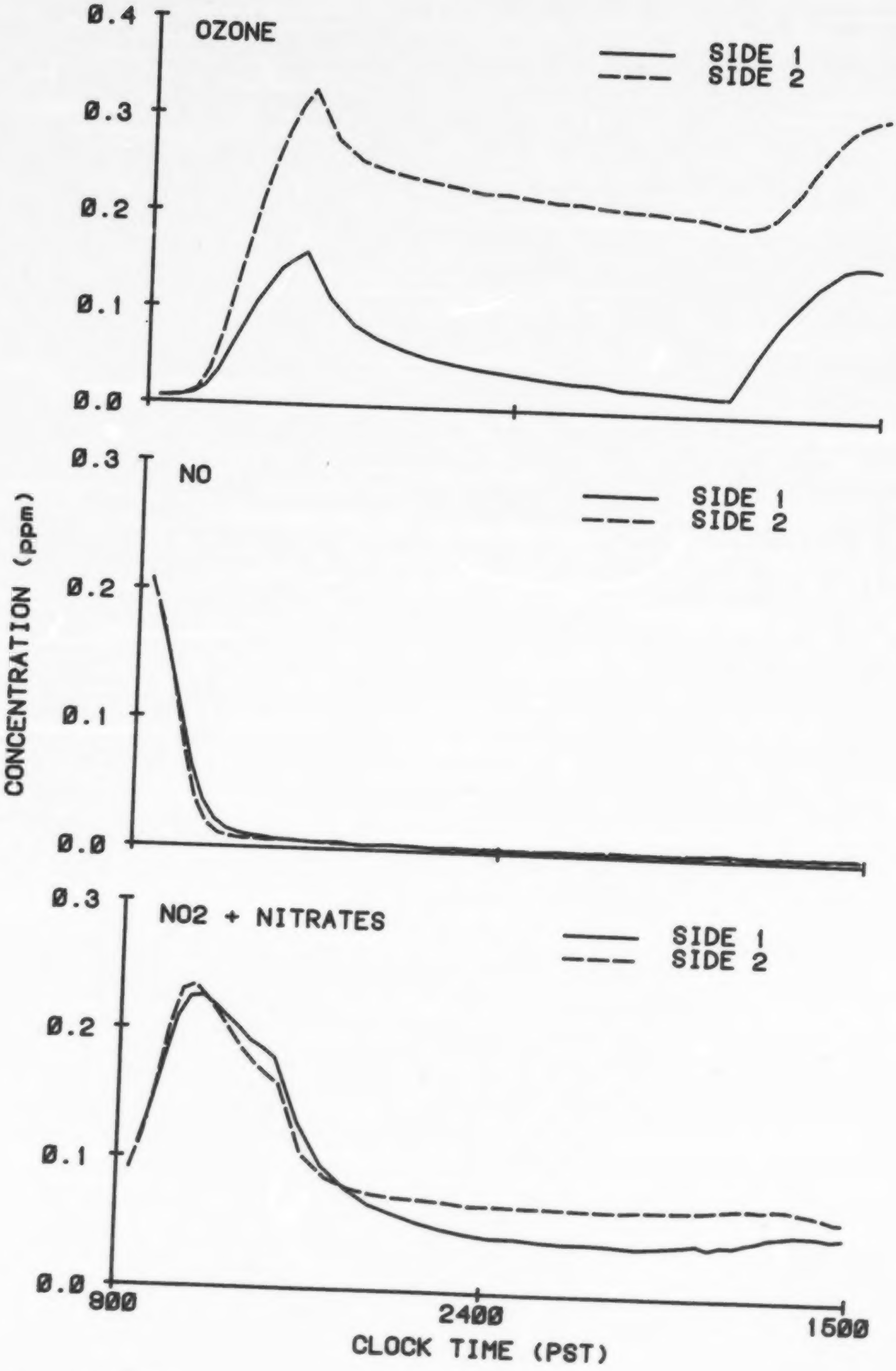


Figure 5. Concentration-time plots for selected species measured in surrogate vs surrogate side equivalency test run OTC-163.

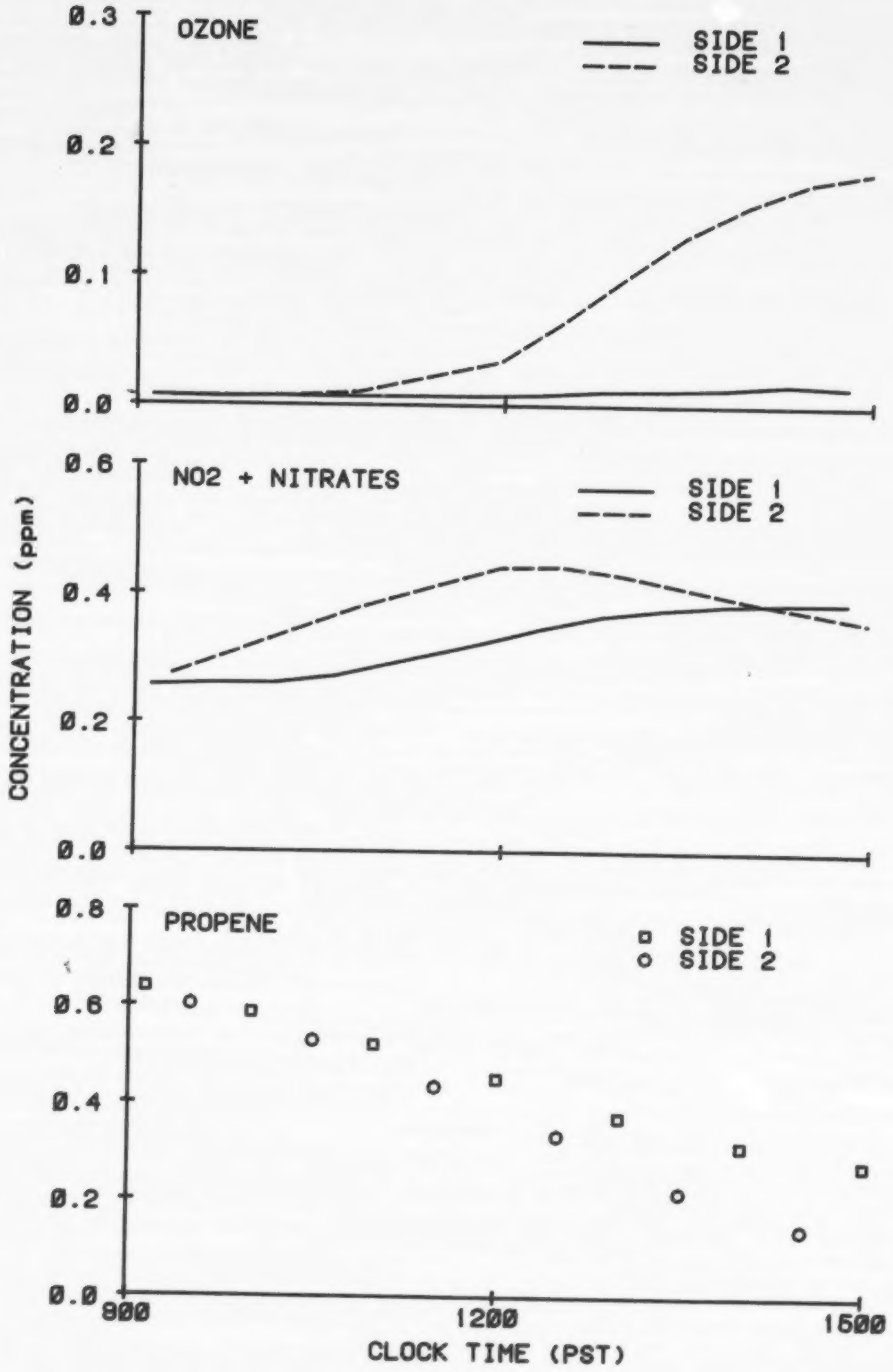


Figure 6. Concentration-time plots for selected species measured in propene vs propene side equivalency test run OTC-169.

Table 9. Brief Summary of Chamber History and Results of Side Equivalency Tests for Bags #26 and #27

OTC	Side 1					Side 2				
Run	East		South			West		North		
No.	Surface[a] A	Surface B	Surface A	Surface B	Undivided	Surface A	Surface B	Surface A	Surface B	Remarks
146					CH_3CHO					New Bag #26
147					O_3 (dark)					
148					C_3H_6-NO_x					
149	CO						Air			
150	CO-NO_x *[b]	-	-	-	-	-	NO_x	-	-	Side 1 anomalously reactive
151	Surg-NO_x[c]	-	-	-	-	-	Surg-NO_x[c]	-	-	Side 2 more reactive
152	NO_x	-	-	-	-	-	NO_x	-	-	Sides nearly equivalent
153			-	-	Surg-NO_x					2-day conditioning
155	NO_x	-	-	-	-	-	NO_x*	-	-	Water in bottom of bag - removed before run. Side 2 anomalously reactive
157	Surg-NO_x	-	-	-	-	-	Surg-NO_x	-	-	Side 2 more reactive
158					O_3 (dark)					New Bag #27
159	C_3H_6-NO_x	-	-	-	-	-	C_3H_6-NO_x	-	-	Nearly equivalent. Side 2 may be slightly more reactive at end
160	NO_x	-	-	-	-	-	NO_x	-	-	Equivalent
161					Air					
162	NO_x	-	-	-	-	-	NO_x	-	-	Equivalent
163	Surg-NO_x	-	-	-	-	-	Surg-NO_x	-	-	Side 2 (surface B) more reactive
165[d]	-	Surg-NO_x	-	-	-	Surg-NO_x	-	-	-	Side 2 (surface A) more reactive
										Background Modified
166	-	Surg-NO_x	-	-	-	Surg-NO_x	-	-	-	Side 2 still more reactive

(continued)

Table 9 (continued) - 2

	Side 1					Side 2				
	East		South			West		North		
OTC Run No.	Surface[a] A	Surface B	Surface A	Surface B	Undivided	Surface A	Surface B	Surface A	Surface B	Remarks
										Foreground Modified-Normal Background
167	-	Surg-NO_x	-	-	-	$\underline{\text{Surg-}NO_x}$	-	-	-	Side 2 still more reactive
										Normal Foreground and Background
168	-	NO_x	-	-	-	$\underline{NO_x}$	-	-	-	Side 2 slightly more reactive, but not anomalous
169	-	C_3H_6-NO_x	-	-	-	$\underline{C_3H_6\text{-}NO_x}$	-	-	-	Side 2 more reactive
170[e]	-	-	-	C_3H_6-NO_x	-	-	-	$\underline{C_3H_6\text{-}NO_x}$	-	Side 2 (surface A) still more reactive
171[d]	-	-	$\underline{C_3H_6\text{-}NO_x}$	-	-	-	-	-	C_3H_6-NO_x	Side 1 (surface A) more reactive
172					C_3H_6-NO_x					
173	-	-	$\underline{C_3H_6\text{-}NO_x}$	-	-	-	-	-	C_3H_6-NO_x	Side 1 still more reactive
										Chamber Relocated
174	-	-	-	-	C_3H_6-NO_x	-	-	-	-	
175[e]	$\underline{C_3H_6\text{-}NO_x}$	-	-	-	-	-	C_3H_6-NO_x	-	-	Side 1 (surface A) still more reactive, but effect is much less

---

[a] "A" or "B" indicates bag surface to which the reactants were exposed.

[b] Underline indicates mixture more reactive than equivalent mixture on other side. Asterisk indicates anomalous reactivity.

[c] For all surrogate runs listed in this table (including the undivided bag run OTC-153), the liquid components of the surrogate were injected through the port of side 2, while the gaseous components, were injected on side 1, prior to bag division.

[d] Bag flipped in frame. Surfaces on opposite sides than previously.

[e] Frame rotated. Side number of bag surface not changed.

with bag #28 (see Table 2). For example, Figure 7 shows the concentration-time profiles measured during the surrogate vs surrogate run OTC-182, the last run carried out using bag #28. With bag #29 (the only bag employed during the 1983 series of outdoor experiments), the first side equivalency test (run OTC-189, Table 2) indicated that side 1 may be slightly more reactive, though the difference was much smaller than was the case with bags #26 and #27. The run was repeated with sides reversed, and the side with the more reactive surface in run OTC-189 was also the more reactive in run OTC-190, despite being on the opposite side of the frame, though the magnitude of the discrepancy was less. This suggests a contamination problem in this case; and, after the bag was conditioned with an undivided propene-NO_x-air irradiation (run OTC-191), it exhibited good equivalency in run OTC-192 (see Table 2). Following a series of runs in which either the initial surrogate, the initial NO_x, or both, were varied, the side equivalency was tested again in run OTC-199, and was still found to be good. Thus a lack of side equivalency did not appear to be a significant problem during the time most of the experimental runs in 1983 were carried out.

It should be noted that the relocation of the chamber was not the only significant difference between the conditions of the experiments carried out using bags #26 and #27 (where side equivalency was a problem) and those carried out using bags #28 and #29 (where it was not). As discussed in Section II.B.2, for all the surrogate experiments in the 1982 series using bags #26 and #27, the liquid components of the surrogate were injected through a port on side 2, while the gaseous components were injected through side 1. Although this was prior to the time the bag was divided, some of the less volatile liquid components might have tended to be preferentially absorbed on the walls on side 2, causing that side to be more reactive after the bag was divided. Indeed, this explanation is consistent with practically all of the data discussed in this section. Note in particular the following: (1) In all surrogate vs surrogate side equivalency tests, the surrogate-NO_x-air mixture on side 2 was the more reactive, even when the bag was rotated within the frame. (2) When a propene-NO_x-air mixture was used for the side equivalency test, the more reactive side was consistently the side whose surface had been on side 2 during the last surrogate run (i.e., surface "A" in surrogate vs surrogate

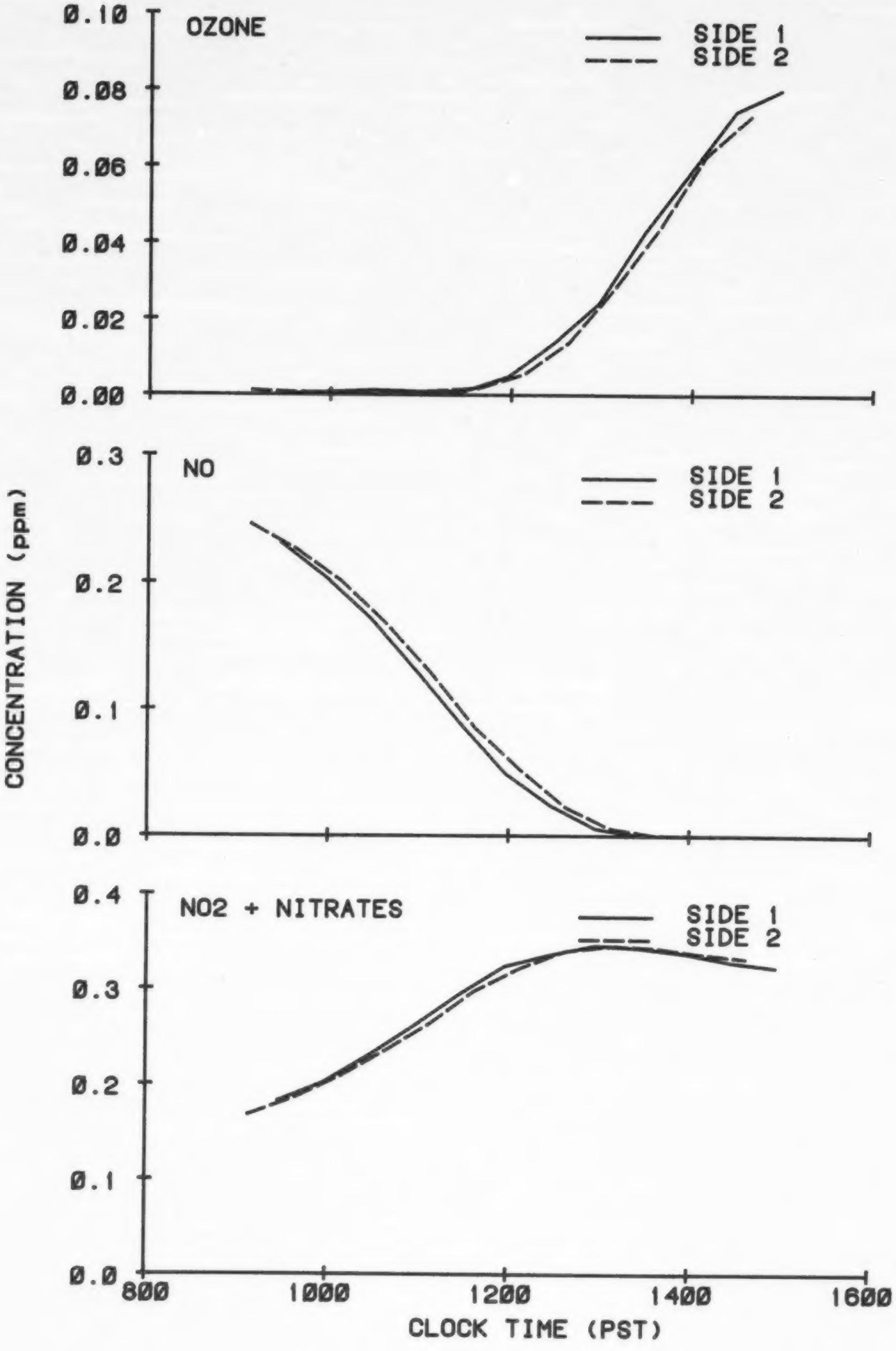


Figure 7. Concentration-time plots for selected species measured in surrogate vs surrogate side equivalency test run OTC-182.

run OTC-167), even in experiments when the bag was rotated in the frame and that surface was on side 1 of the frame. (See results of runs OTC-169, 170, 171, 173 and 175, in Table 9, in which surface "A" was consistently the more reactive). (3) The propene vs propene side equivalency tests carried out before the bag was exposed to the surrogate mixture (run OTC-159 in bag #27 and runs OTC-178 and 179 in bag #28) all exhibited good side equivalency. (4) In the first surrogate vs surrogate run carried out using bag #28, (run OTC-181, Table 2) the injection procedure was modified so all surrogate components were injected equally through each side, and that was the first surrogate vs surrogate run in which acceptable side equivalency was observed. Finally (5) the fact that side inequivalency was less of a problem during the 1983 series can be attributed to the fact that a different injection procedure for the liquid (and gaseous) surrogate components, involving use of compressed gas tanks carrying mixtures of the vapors in N_2, rather than evaporating the liquid components (see Section II.A.2), was employed during the 1983 series.

However, the existing data do not unambiguously prove that the above-discussed explanation was the source of the inequivalency problem observed during the 1982 series, and the results of one experiment, surrogate vs surrogate run OTC-182, is not totally consistent with that explanation. In that run, carried out in bag #28 immediately following the run (i.e., OTC-181 dicussed above) where the surrogate was injected equally into each side, the surrogates were injected in the manner used for the 1982 series runs (i.e., unequally), but good side equivalency was still observed (see Figure 7). It is possible that the previous equal exposure to surrogate mixture in the preceding two runs (run OTC-180 was aborted due to weather after the surrogate components had been injected equally into each side) lessened the impact of the unequal injection on the surrogate components in run OTC-182. If this was indeed the case, then equal conditioning of both sides of new Teflon bag reactors with all surrogate components employed is critical to assure good side equivalency in subsequent runs. However, as indicated above, this explanation has not been unambiguously shown to be true, and the actual cause of the side-inequivalency problem which plagued the 1982 series of outdoor experiments must be considered to be uncertain.

7. Light Intensity Measurements

As discussed in Section II.C.4, the light intensity in the outdoor chamber experiments was measured using two different techniques, one employing a UV radiometer mounted on the roof of the building containing the monitoring instruments, and the other involving direct measurements of the NO_2 photolysis rate (k_1) using a quartz tube located beneath the reaction bag. A set of these data are shown in Figure 8 for a representative multi-day outdoor irradiation (run OTC-202). It can be seen from Figure 8 that the UV measurements are available at much more frequent intervals than was the case of the k_1 data, and are thus more useful for monitoring relative changes of light intensity throughout the day. However, it is the NO_2 photolysis rates that are more directly relevant to the photochemical processes of interest in environmental chamber experiments, and the radiometric UV measurements are primarily useful insofar as they reflect instantaneous changes in the k_1 values.

Relationships between NO_2 photolysis rates and radiometric UV measurements have been discussed previously, and a number of empirical relationships have been derived (Zafonte et al. 1977, Jeffries et al. 1982, Madronich et al. 1983). In general, the factor relating these measurements was found to depend on the solar Zenith angle, Z, and we found this also to be the case for the data obtained in this study. Although there is some degree of scatter in the data, presumably as a result of differing effects of clouds, haze, etc., on these measurements, as well as imprecision in the data themselves. The ratios of the k_1/UV measurements made at the same time could be fit by the following approximate linear relationship derived by least squares regression:

$$k_1(\text{min}^{-1})/\text{UV}\ (\text{mW cm}^{-2}) = (0.090 \pm 0.002) - (0.016 \pm 0.003) \cos(Z), \qquad \text{(IX)}$$

and a plot of the k_1 values calculated from the UV measurements against the observed k_1 values is shown in Figure 9. Our data are not sufficiently precise to indicate a more complex relationship, and thus we recommend using equation (IX) to estimate k_1 values from UV measurements when no k_1 data are available.

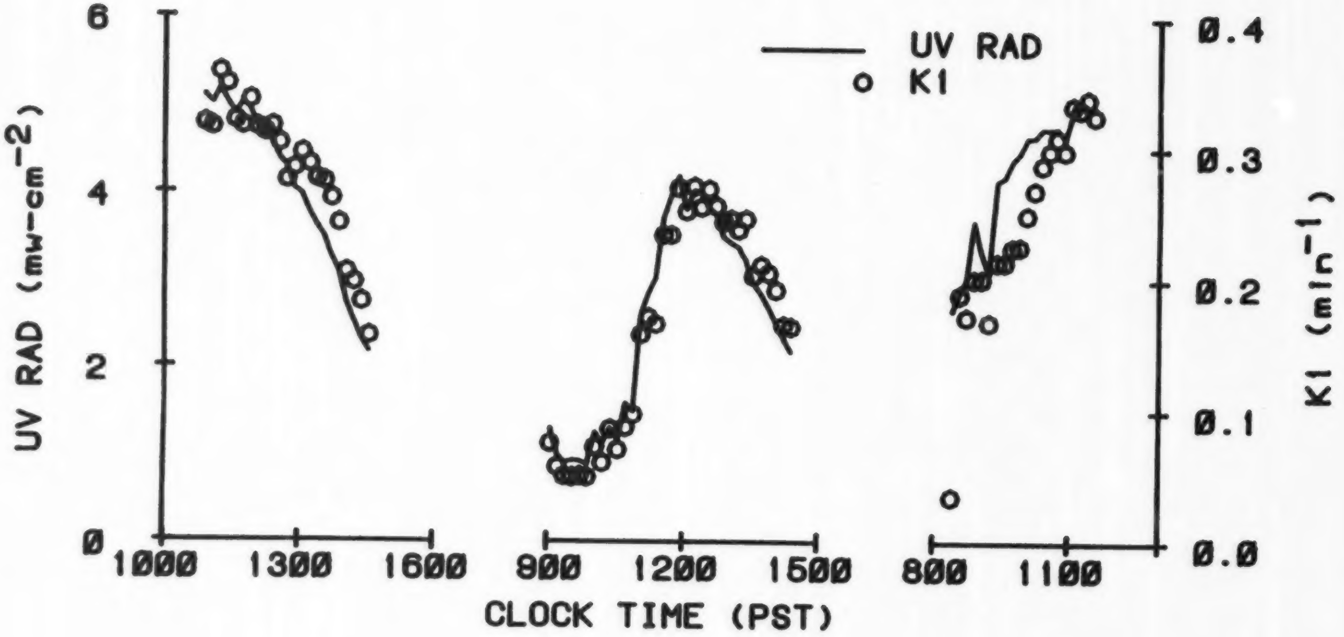


Figure 8. Plot of UV radiometer (——) and k_1 (0) data for multi-day surrogate run OTC-202.

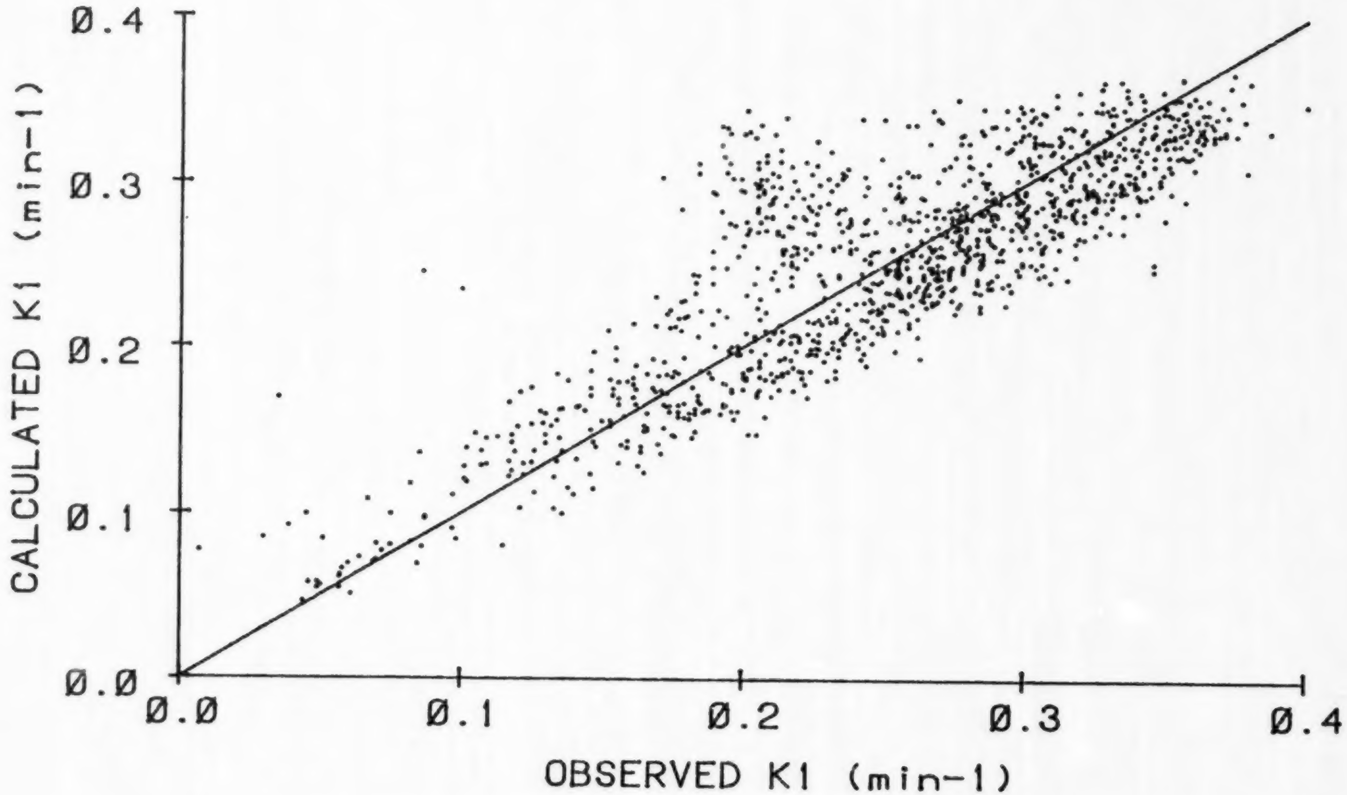


Figure 9. Plot of k_1 values calculated from the radiometric UV measurements using equation (IX) against the measured k_1 values. Line shown is for calculated = observed (i.e., of unit slope).

The experimental k_1 measurements can also be compared with theoretically calculated values, based on the known absorption cross-sections and photodissociation quantum yields for NO_2 (NASA 1983) and estimated actinic irradiances for clear sky conditions (Peterson 1976), which depend on the solar Zenith angle. Since the calculated k_1 values are appropriate only for clear sky conditions, they should strictly be considered to be upper limits to the experimental values. This is indeed the case, and is shown in Figure 10, which shows plots of the experimental and theoretically calculated k_1 values against the cosine of the solar Zenith angle. The upper limits of the experimental k_1 values have a similar dependence on the solar Zenith as do the theoretical values, but the experimental upper limits are consistently ~20-25% lower than the theoretical values. This could be attributed in part to uncertainties in the estimated actinic irradiations (particularly regarding the role of surface albedo) as it applies to the site of our experiments, but a more obvious explanation comes from the fact the quartz tube used to measure the k_1 values was located underneath the chamber, so the sunlight passed through two layers of Teflon film before reaching the tube. This could reasonably be expected to cause a ~20% reduction in the light intensity. If this is the case, then the actual light intensity within the reaction chamber would be ~10% higher than that measured beneath the chamber. Thus the experimental k_1 values appear to be reasonably consistent with those expected.

8. Results of Surrogate-NO_x-Air Irradiations

The results of all surrogate-NO_x-air irradiations carried out during the two phases of the outdoor chamber program are summarized in Tables 10 and 11. Essentially four types of surrogate-NO_x-air irradiations were carried out: (1) Side equivalency tests, whose results were discussed above in Section III.A.6.; (2) run OTC-153, carried out to condition the bag after our initial observation of side inequivalency; (3) run OTC-196, conducted in such a manner that the NO_x-offgassing rate on day 2 could be measured while the run was underway and whose results are discussed above in Section III.A.1; and (4) a series of divided chamber runs where the initial levels of surrogate and/or NO_x were varied, and in some cases where NO was injected on subsequent days of the run to regenerate photochemical reactivity. In this section, the results of these

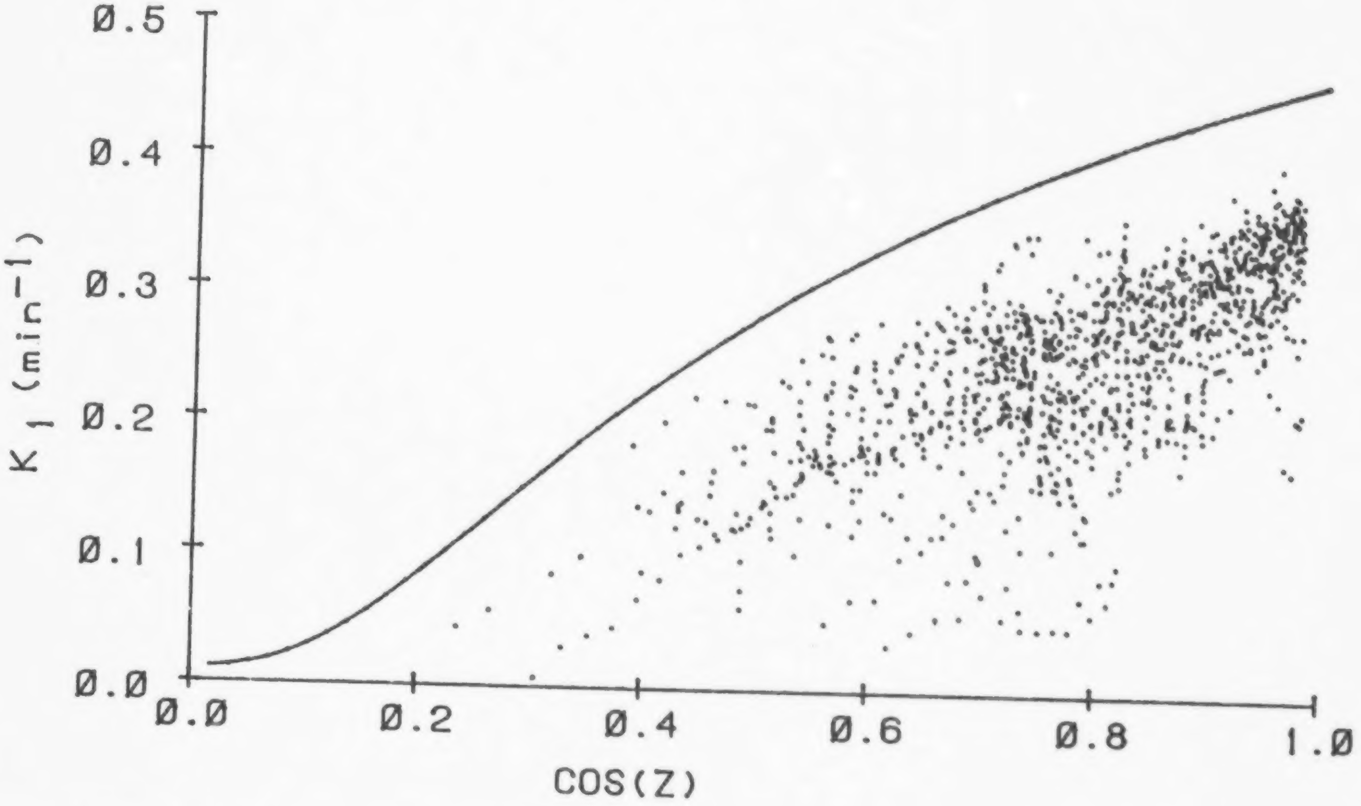


Figure 10. Plots of experimental (·) and theoretically calculated (——) k_1 values against solar Zenith angle.

Table 10. Results of Surrogate-NO_x-Air Irradiations in the Outdoor Chamber During the Fall-Winter of 1982

OTC Run Number	151		153	157		163		165		166		167		181		182	
Conditions[a]	New							A		A,B		C		D,E		D,E	
Side	1	2	Undiv.	1	2	1	2	1	2	1	2	1	2	1	2	1	2
Initial NO (ppm)	0.22		0.31	0.30		0.21		0.25		0.21		0.22		0.26		0.25	
NO_2 (ppm)	0.10		0.10	0.09		0.09		0.10		0.13		0.08		0.15		0.16	
Surrogate (ppmC)	1.71		2.24	3.02		2.25		2.65		2.47		2.31		3.42		3.20	
Day 1																	
Time uncovered (PST)	1037		0930	0935		0900		1020		0950		0914		0911		0859	
Final O_3 (ppm)	0	0	0.14	0.04	0.34	0.16	0.33	0.10	0.21	0.01	0.08	0.02	0.16	0.07	0.07	0.09	0.09
NO_x + nitrates (ppm)	0.27	0.28	0.20	0.19	0.18	0.18	0.16	0.24	0.21	0.30	0.27	0.25	0.21	0.32	0.31	0.31	0.32
PAN (ppb)	1	1	11	10	65	14	43	13	39	2	17	3	29	35	38	-	-
HCHO (ppm)	0.04	0.04	0.11	0.19	0.09	0.10	0.12	0.14	0.13	0.05	0.14	0.10	0.02	0.13	0.08	-	-
Time covered (PST)	-		-	-		1530		1520		1500		1500		~1600		1608	
Average[b] k_1 (min^{-1})	-		-	-		-		-		-		-		0.16±0.06		0.12±0.06	
UV ($mW\ cm^{-1}$)	0.7±0.3		3.1±0.8	3.8±0.9		3.3±0.8		3.3±0.8		1.9±0.8		3.1±0.6		-		-	
T (C)	26±2		38±4	26±3		38±5		30±3		27±3		28±3		19±4		21±5	
Day 2																	
Initial O_3 (ppm)	0	0	0.02	[c]	0.18	0.02	0.20							0.01	0.01		
NO_x + nitrates (ppm)	0.26	0.28	0.05		0.08	0.04	0.07							0.15	0.17		
PAN (ppb)	2	7	16		77	14	65							40	38		
HCHO (ppm)	0.08	0.02	0.09		0.20	0.11	0.12							0.11	0.11		
Time uncovered (PST)	-		-	-		0900								0907			
Final O_3 (ppm)	0.10	0.30	0.21			0.16	0.31							0.24	0.18		
NO_x + nitrates (ppm)	0.12	0.11	0.07			0.05	0.06							0.11	0.11		
PAN (ppb)	9	34	10			13	27							104	100		
HCHO (ppm)	0.13	0.12	0.09			0.18	0.17							0.10	0.12		
Time covered (PST)	-		1350			1520								1502			
Average k_1 (min^{-1})	-		-			-								0.15±0.04			
UV ($mW\ cm^{-2}$)	3.0±0.9		3.4±0.4			3.0±0.9								-			
T (C)	34±4		39±4			34±5								19±4			
Day 3																	
Initial O_3 (ppm)	~0	0.22															
NO_x + nitrates (ppm)	0.02	0.01															
PAN (ppb)	2	33															
HCHO (ppm)	0.08	0.09															
Time uncovered (PST)	-																
Final O_3 (ppm)	0.11	0.23															
NO_x + nitrates (ppm)	0.01	0.01															
PAN (ppb)	13	21															
HCHO (ppm)	0.04	0.02															
Time covered (PST)	1530																
Average UV ($mW\ cm^{-2}$)	2.4±1.1																
T (C)	27±3																

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[a] Special condition codes:

New - Newly conditioned bag; not previously used for surrogate irradiation.

A - Bag orientation changed 180° relative to that in previous runs, and flipped top/bottom. Bag surface previously on east side of frame (side 1), now on west side (side 2).

B - Three large canvas-like tarps were hung behind the chamber to provide more uniform reflection of sunlight into the chamber.

C - Tarps removed. Carpet normally under chamber removed. Large van moved in front of chamber so reflected light from foreground would appear to be more equal.

D - Chamber relocated 20 feet to the west relative to its position on run OTC-167 and those previous. Normal orientation and conditions otherwise.

E - Unpolluted morning air used because of pure air system malfunction.

[b] Average given from time bag uncovered to time covered on that day. If bag not uncovered, average starts at 0900 PST, if not covered, average ends at 1530 PST.

[c] Side deflated.

Table 11. Results of Multi-Day Surrogate-NO$_x$-Air Irradiations in the Outdoor Chamber During the Summer-Fall of 1983

OTC Run Number	189		190		192		194		195		196	197		198		199		202		203		204		205		205	
Side	1	2[a]	1	2	1	2	1	2	1	2	2[b]	1	2	1	2[a]	1	2	1	2	1	2	1	2	1	2	1	2
Initial:																											
NO (ppm)	0.35		0.29		0.28		0.24		0.25		0.31	0.24	0.56	0.45	0.13	0.28		0.62	0.31	0.30	0.14	0.30	0.13	0.69	0.10		
NO$_2$ (ppm)	0.10		0.13		0.19		0.15		0.16		0.10	0.14	0.22	0.39	0.26	0.09		0.16	0.08	0.09	0.04	0.09	0.05	0.15	0.04		
Surrogate (ppmC)	3.98		3.64		3.95		6.87	3.55	1.83	4.04	3.58	3.59		5.23[c]	3.48	3.51		6.86	2.82	3.48		3.44		3.59			
Day 1																											
Time uncovered (PST)	0915		0915		0915		0940		1020		1000	1000		1015		0945		1045		0956		1000		1056			
Final:																											
O$_3$ (ppm)	0.58	0.71	0.70	0.67	0.74	0.75	0.73	0.60	0.16	0.68	0.60	0.62	0.14	0.70	0.67	0.59	0.59	0.68	0.52	0.23	0.39	0.30	0.38	0.04	0.39		
NO$_x$ + nitrates (ppm)	0.18	0.18	0.14	0.15	0.18	0.19	0.20	0.21	0.28	0.18	0.20	0.17	0.50	0.39	0.18	0.17	0.17	0.30	0.19	0.26	0.11	0.20	0.09	0.56	0.09		
PAN (ppb)	21	25	18	18	56	58	40	55	7	55	-	62	10	87	59	57	55	86	46	16	26	49	61	10	46		
HCHO (ppm)	0.04	0.16	0.28	0.21	0.21	0.25	0.23	0.13	0.07	0.17	0.21	-	0.20	0.37	0.17	0.20	0.22	0.22	0.11	0.18	0.22	0.25	0.17	0.18	0.22		
Time covered (PST)	1515		1515		1515		1510		1518		1500	1524		~1530		1550		1542		1520		1530		1545			
Average k_1 (min^{-1})	0.32±0.04		-		0.31±0.05		0.32±0.04		0.28±0.02		0.26±0.28	0.29±0.04		0.24±0.06		0.25±0.04		0.28±0.05		0.19±0.08		0.18±0.05		0.23±0.04			
Average UV (mW cm^{-2})	3.9±0.5		3.8±0.9		4.1±0.6		4.2±0.5		3.8±0.5		3.5±0.4	3.8±0.7		3.4±0.8		3.3±0.6		3.2±0.8		2.4±0.8		2.4±0.7		2.8±0.8			
Average T (C)	38±3		41±5		39±3		36±4		36±4		42±6	33±5		38±3		35±4		36±4		27±2		31±3		32±4			
Day 2																											
Initial:																											
O$_3$ (ppm)	0.27	0.45	0.46	0.42	0.41	0.48	0.46	0.41	0.01	0.43	0.32	0.40	0.01	0.32	0.48	0.38	0.41	0.31	0.30	0.05	0.30	0.12	0.27	0.01	0.28		
NO$_x$ + nitrates (ppm)	0.08	0.08	0.08	0.08	0.08	0.09	0.11	0.12	0.14	0.10	0.06	0.10	0.38	0.19	0.12	0.08	0.09	0.17	0.11	0.09	0.08	0.09	0.03	0.53	0.07		
PAN (ppb)	8	7	2	2	12	8	10	14	20	9	17	27	24	72	21	17	20	58	27	0.22	-	50	35	10	30		
HCHO (ppm)	-	-	0.15	0.14	0.28	0.28	0.37	0.18	0.16	0.19	-	-	-	0.29	0.15	0.28	0.26	0.22	0.15	-	-	0.20	0.19	0.07	0.10		
Time uncovered (PST)	0900		0900		0900		0900		0900		1015	0900		0855		0900		0900		[d]		1000		0859			
NO injected (ppm)	-		-		-	~0.14	-		-		-	-	-	-		-	~0.15	-				-		-	0.11		
Time NO injected (PST)	-		-		-	1032	-		-		-	-	-	-		-	1000	-				-		-	1009		
Final:																											
O$_3$ (ppm)	0.35	0.35	0.34	0.35	0.28	0.64	0.37	0.47	0.40	0.42	0.37	0.40	0.65	0.52	0.40	0.38	0.59	0.37	0.31			0.20	0.25	0.46	0.51		
NO$_x$ + nitrates (ppm)	0.07	0.07	0.05	0.06	0.11	0.16	0.11	0.09	0.11	0.10	0.06	0.12	0.21	0.17	0.12	0.09	0.14	0.19	0.14			0.10	0.09	0.28	0.15		
PAN (ppb)	4	4	2	2	7	23	7	7	10	7	8	16	24	26	10	9	30	46	21			53	45	41	49		
HCHO (ppm)	0.11	0.08	0.14	0.11	0.07	0.10	0.10	0.09	0.05	0.10	0.17	0.22	0.14	0.22	0.14	0.12	0.10	0.15	0.09			0.11	0.11	0.10	0.10		
Time covered/ terminated (PST)	1500		1500		1510		1500		1500		1515	1525		1519		1520		1530				1530		1525			
Average k_1 (min^{-1})	0.29±0.05		0.32±0.05		0.32±0.05		0.26±0.04		0.28±0.04		0.15±0.04	0.26±0.05		0.25±0.06		0.26±0.06		0.16±0.08				0.20±0.06		0.25±0.04			
Average UV (mW cm^{-2})	4.2±0.5		4.0±0.5		4.1±0.5		4.1±0.5		3.9±0.5		3.9±0.6	3.5±0.6		3.6±0.9		3.5±0.8		1.9±0.9				2.5±0.8		3.0±0.6			
Average T (C)	40±6		42±4		43±4		38±4		37±4		39±2	33±5		37±4		37±3		28±5				28±3		39±2			
Days 3 & 4																								Day 3		Day 4	
Initial:																											
O$_3$ (ppm)									0.21	0.36		0.30	0.44	0.39	0.34			0.24	0.23			0.11	0.18	0.21	0.36	0.21	0.31
NO$_x$ + nitrates (ppm)									0.02	0.03		0.09	0.13	0.09	0.08			0.13	0.09			0.08	0.06	0.14	0.11	0.09	0.08
PAN (ppb)									3	1		3	15	3	1			16	7			46	27	31	20	17	34
HCHO (ppm)									0.17	0.08		-	-	-	-			0.14	0.10			0.19	0.13	0.10	0.11	0.05	0.09
Time uncovered (PST)									0900			0900		0855				0851				0900		0900		0902	
NO injected (ppm)									-			-		-				-				~0.14	~0.12	-	0.11	-	0.07
Time NO injected (PST)									-			-		-				-				1000		-	1009	-	1014
Final:																											
O$_3$ (ppm)									0.20	0.32		0.23	0.40	0.35	0.30			0.28	0.21			0.35	0.36	0.32	0.44	0.11	0.28
NO$_x$ + nitrates (ppm)									0.02	0.03		0.11	0.15	0.10	0.09			0.05	0.06			0.13	0.12	0.15	0.16	0.11	0.13
PAN (ppb)									3	3		5	13	3	2			20	9			53	46	35	38	39	57
HCHO (ppm)									0.05	0.17		0.21	0.15	0.27	0.15			0.12	0.10			0.14	0.11	0.10	0.10	0.11	0.06
Time covered/ terminated (PST)									1244			1100		1000				1220				1510		1530		1400	
Average k_1 (min^{-1})									0.29±0.05			0.24±0.03		0.14±0.07				0.24±0.07				0.25±0.25		0.23±0.05		0.21±0.04	
Average UV (mW cm^{-2})									4.5±0.2			3.5±0.4		2.5±0.6				3.4±0.6				3.0±0.6		2.9±0.8		2.9±0.3	
Average T (C)									44±4			33±2		31±1				28±4				37±7		41±5		32±4	

[a] Low bag volume on day 2 due to leakage.

[b] Undivided bag on day 1. Surrogate on side 2 only for day 2.

[c] Amounts of isooctane, n-pentane, toluene and m-xylene relative to other reactants are abnormal due to injection error.

[d] Aborted on beginning of second day due to rain. "Initial" day 2 values taken ~0700-0800 PST.

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experimental runs (other than those carried out for chamber characterization which are discussed in previous sections) are discussed.

As can be seen from Tables 10 and 11, a number of different runs involved irradiation, either on one side of the divided chamber or in the undivided chamber, of a ~3.5 ppmC surrogate, ~0.4 ppm NO_x "standard" surrogate mixture, with the average temperature (for the first day) ranging from 19 C to 42 C, and the average k_1 ranging from 0.12 min^{-1} to 0.32 min^{-1}. A comparison of the concentration-time profiles for O_3 and uncorrected NO_2 for these irradiations is shown in Figure 11. It can be seen that although some irradiations, specifically OTC-194 to 197 and OTC-199 gave remarkably similar results, other runs, particularly those carried out during the winter months, exhibited significantly lower reactivity.

An obvious explanation for the differences among the results of the standard irradiations shown in Tables 10 and 11 and Figure 11 was due to differences in temperature and light intensity. Thus, Figure 12 shows a plot of the first-day maximum O_3 yield against the first-day average temperature, while Figure 13 gives a comparable plot of the maximum O_3 yield against the average NO_2 photodissociation rate, k_1. It can be seen that a good correlation is obtained in both plots, with the correlation coefficient in both cases being 0.93. However, since in general, temperature and light intensity are also highly correlated (correlation coefficient = 0.86 for those standard runs), these data are not suitable for determining which of these two effects was the more important. However, it is important to note that if two different runs were carried out with similar conditions of temperature and light intensity (as was the case for runs OTC-194 to 197 and OTC-199, and also for runs OTC-181 and 182), then reasonably reproducible results could be obtained in these outdoor chamber experiments.

In addition to the irradiations of the "standard" ~3.5 ppmC surrogate, 0.4 ppm NO_x mixture, irradiations were also carried out in which the concentration of the initial hydrocarbon or the initial NO_x was varied, usually (though not always) with the standard mixture on one side of the divided chamber, and a modified mixture on the other. For example, Figure 14 shows concentration-time profiles for selected species for the variable surrogate runs OTC-194 and 195 (both carried out under similar conditions

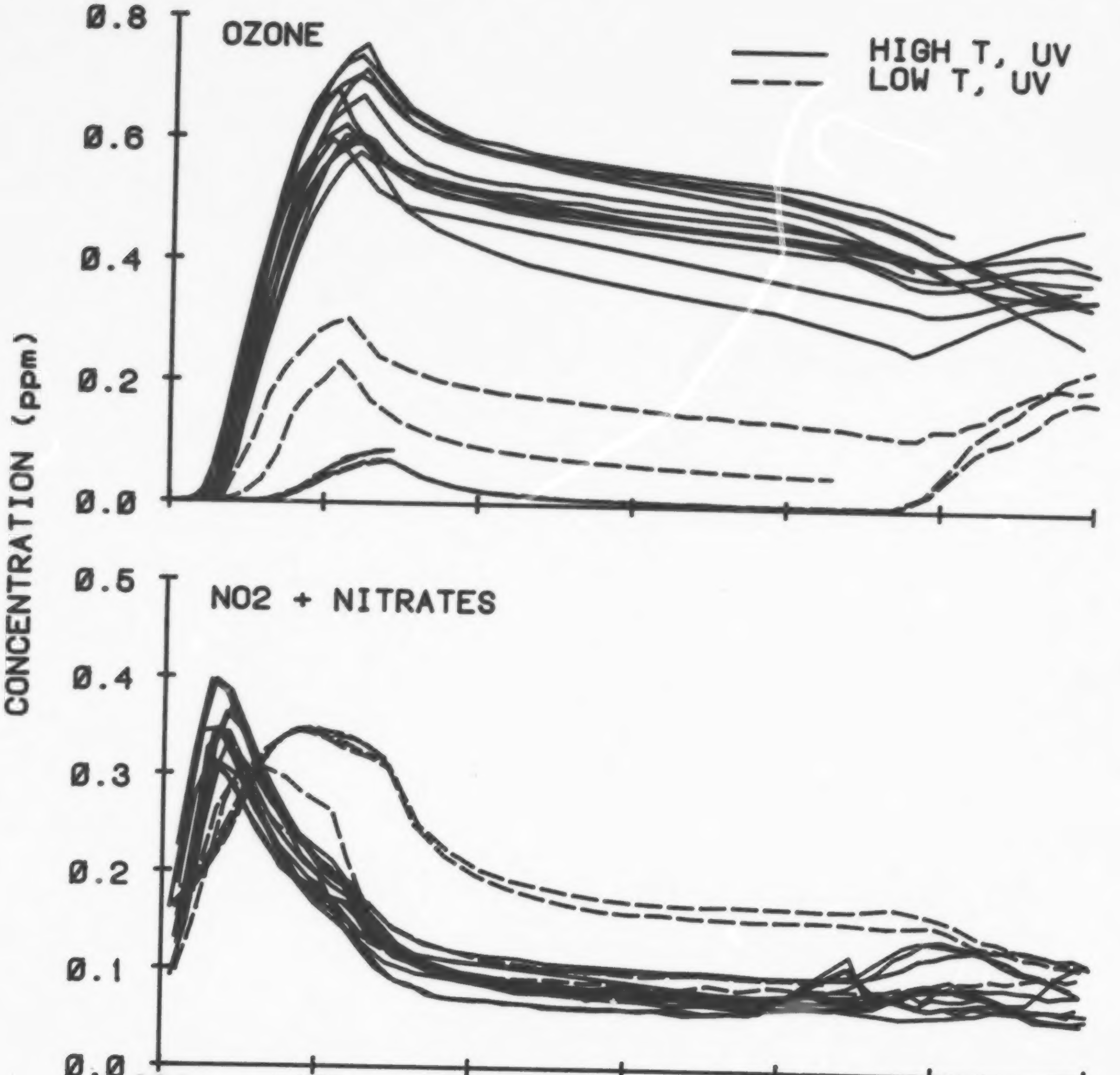

Figure 11. Concentration-time plots for ozone and uncorrected NO_2 for the standard surrogate-NO_x-air irradiations, where the runs are classified as either "high T, k_1" runs (average T >32 C, average k_1 >0.2 min^{-1}) or "low T, k_1" runs (average T, k_1 both below those values).

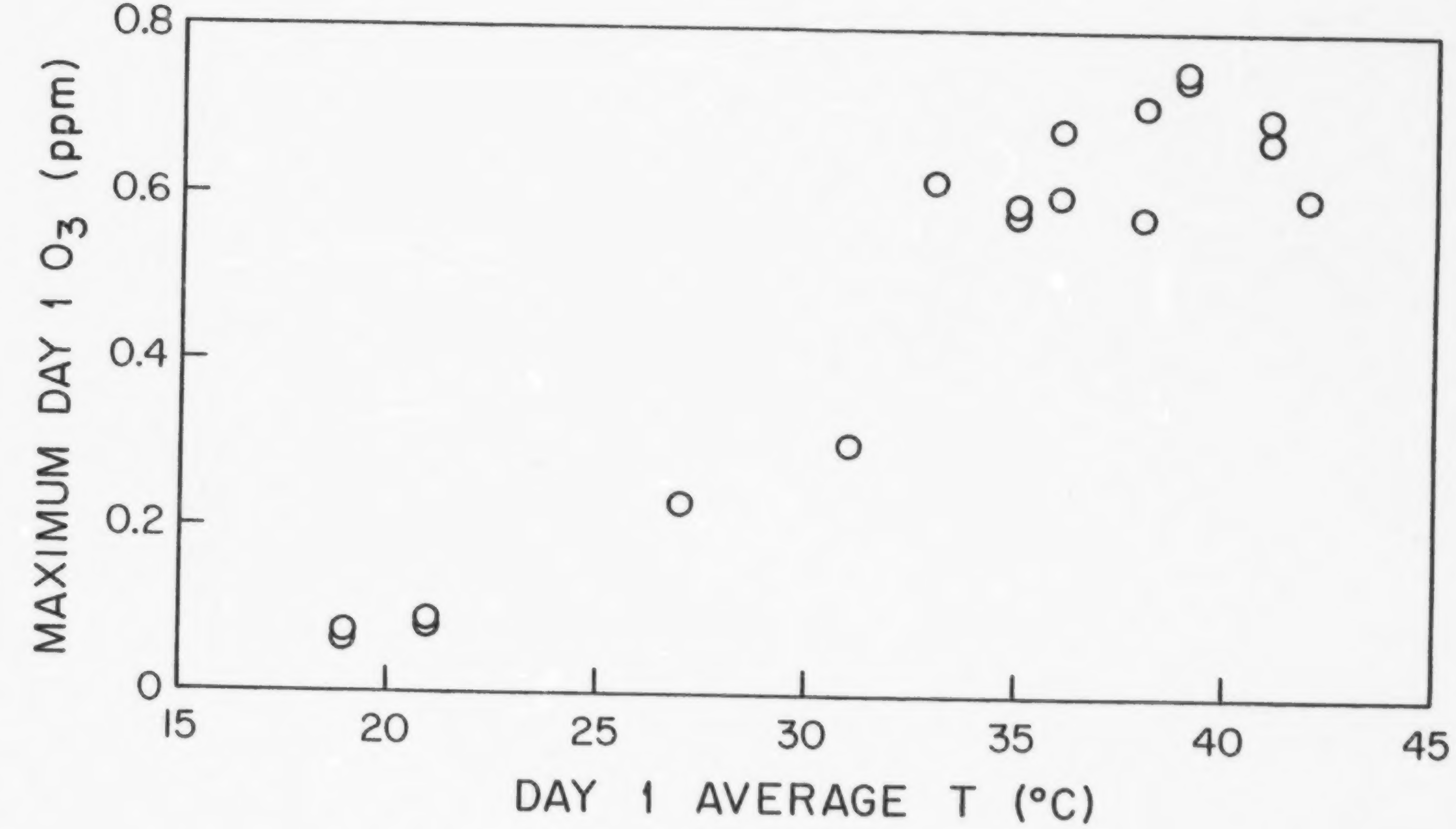

Figure 12. Plot of maximum O_3 yields against average T for the first day of the standard surrogate-NO_x-air irradiations.

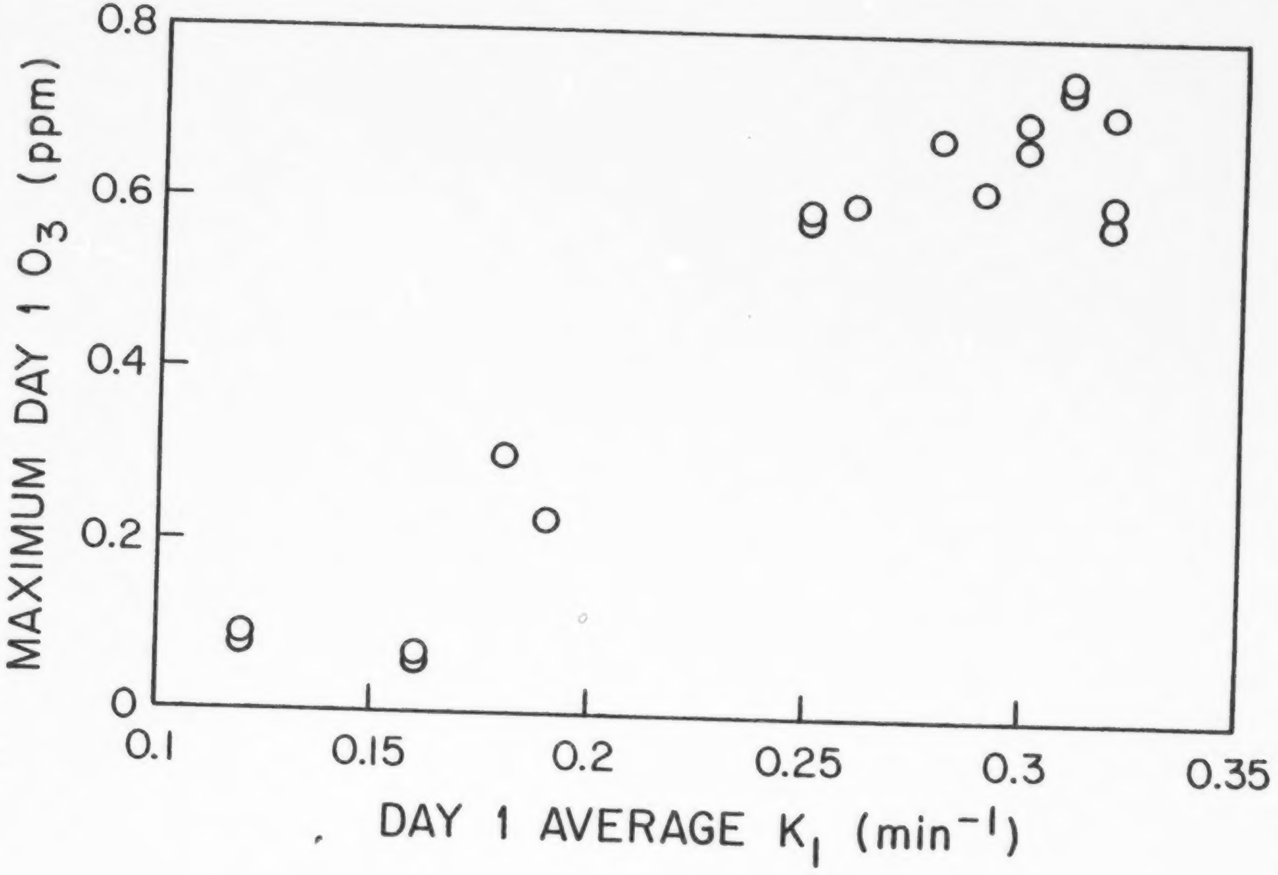

Figure 13. Plot of maximum O_3 yields against average k_1 for the first day of the standard surrogate-NO_x-air irradiations.

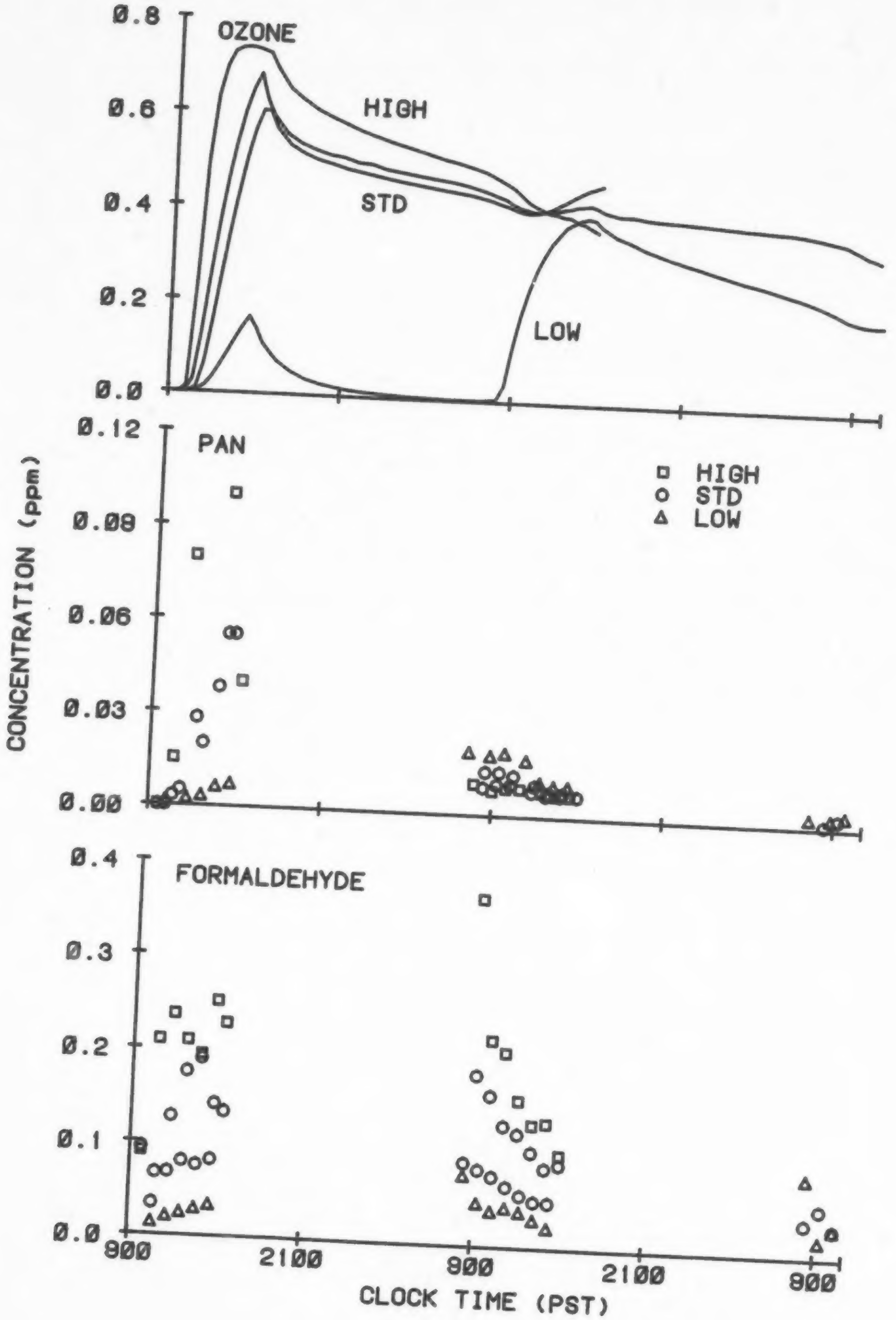

Figure 14. Concentration-time plots of O_3, PAN, and formaldehyde for the variable surrogate runs OTC-194 and 195. "High," "low" and "STD" refers to data for mixtures with initial surrogate levels of ~7, ~2 or ~4 ppmC, respectively.

of temperature and light intensity) and Figure 15 shows selected results for the variable NO_x runs OTC-204 and 205. (In this figure data obtained after subsequent NO_x injections were made are not shown.) As for other such runs carried out in this program, and as expected based on the large body of existing environmental chamber and modeling data available, the reactivity on the first day tended to increase with the initial surrogate concentration and (at least at the reactant levels and conditions employed here) to decrease with increasing initial NO_x. However, as can be seen from these figures (and Table 11), this was not necessarily the case on the second day of the irradiation.

For the "standard" run carried out under conditions of relatively high temperature and light intensity (as was the case for the runs shown in Figures 14), the typical result was for the maximum O_3 formation to occur on the first day. The O_3 concentrations then declined during the night, with only a relatively small increase in O_3 on the second day from its early morning minimum. When the initial surrogate level was increased (run OTC-194, side 1, in Figure 14), more O_3 was formed on the first day, as expected. However, less O_3 was formed on the second day, leading to the apparently anomalous result (at least for run OTC-194) of there being less O_3 on day 2 in the high-surrogate side than on the low surrogate side. This was presumably because more of the NO_x on the high surrogate side was also consumed on the first day. When the initial surrogate was decreased from the standard level (run OTC-195, side 1, Figure 14), much less O_3 was formed on the first day, but in addition less NO_x was consumed. Thus, since there was insufficient O_3 to consume all the remaining NO_x during the night due to the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \overset{M}{\rightleftarrows} N_2O_5$$

$$NO_3 \xrightarrow{wall} \text{loss of } NO_x$$

$$N_2O_5 \xrightarrow{wall} \text{loss of } NO_x$$

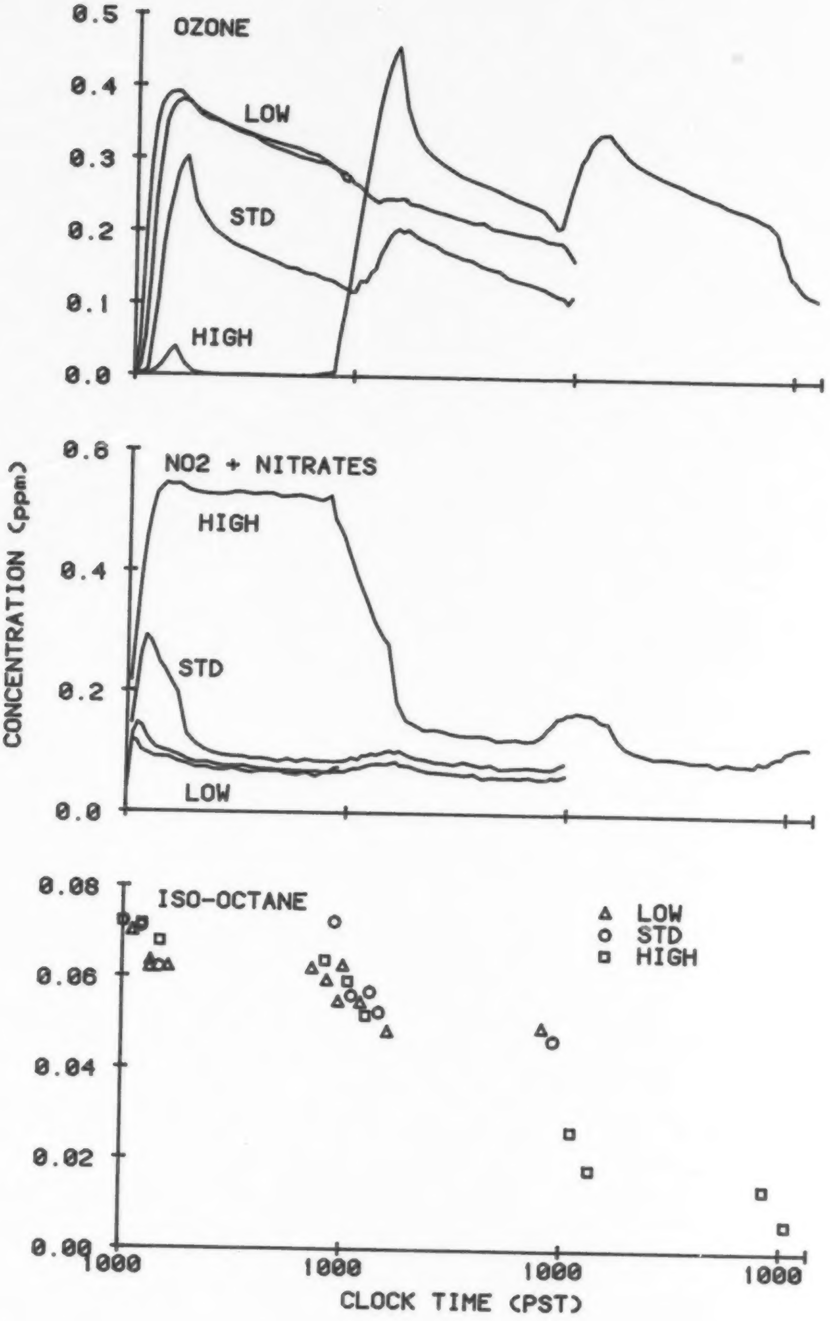

Figure 15. Concentration-time plots for O_3, uncorrected NO_2 and iso-octane for the variable initial NO_x runs OTC-204 and 205. "High," "low" and "STD" refer to curves for mixtures with initial NO_x levels of ~0.8, ~0.2 and ~0.4 ppm, respectively. Data obtained after subsequent NO_x injections not shown.

sufficient NO_x remained the next morning to allow for rapid O_3 formation on day 2, with the maximum second day O_3 on the lower surrogate side approaching the second day ozone levels of the higher surrogate side. Thus in general second day O_3 levels in these types of irradiations were much less sensitive to initial hydrocarbon levels than was the case for O_3 levels on the first day.

These runs also indicated that the effects of varying the initial NO_x concentrations were also significantly different on the second day of the irradiation than on the first. This is shown in Figure 15, which gives selected results from two different runs employing three different initial NO_x levels carried out under similar temperature and light intensity conditions. It can be seen that, as expected, increasing the initial NO_x concentration significantly decreased the O_3 yields on the first day. However, this was not necessarily so for subsequent days, when NO_x remaining in the higher initial NO_x experiments allowed additional O_3 formation to occur. Indeed, at least for the conditions of these experiments, the effect of initial NO_x levels on ozone formation on the second day appeared to be opposite to that on the first day. Thus, increasing the initial NO_x concentrations consistently increased the maximum yields of O_3 on the second day of these irradiations. In addition, for the highest NO_x/hydrocarbon experiment (side 1 of run OTC-205), significant NO_x formation also occurred on the third day. Unless NO was added this did not occur for the other experiments.

In some experiments, fresh NO was added on the second and/or subsequent days of the irradiations to determine its effect on ozone formation. For example, in run OTC-199, a side equivalency test consisting of an irradiation of the same standard surrogate mixture on day 1, ~0.15 ppm of NO was added to side 2 near the beginning of the second day of the run, and selected concentration-time plots for that run are shown in Figure 16. It can be seen that, while the addition of NO caused an initial large drop in the O_3 level, due to the rapid reaction between O_3 and NO, rapid O_3 formation subsequently occurred, resulting in much higher O_3 levels at the end of the day than for the side without added NO, where no photochemical O_3 formation occurred. In run OTC-205, where the initial NO_x was ~0.8 ppm on side 1 and ~0.2 ppm on side 2 (with similar surrogate levels on both sides), ~0.1 ppm of NO was added to the low NO_x side on days 2, 3

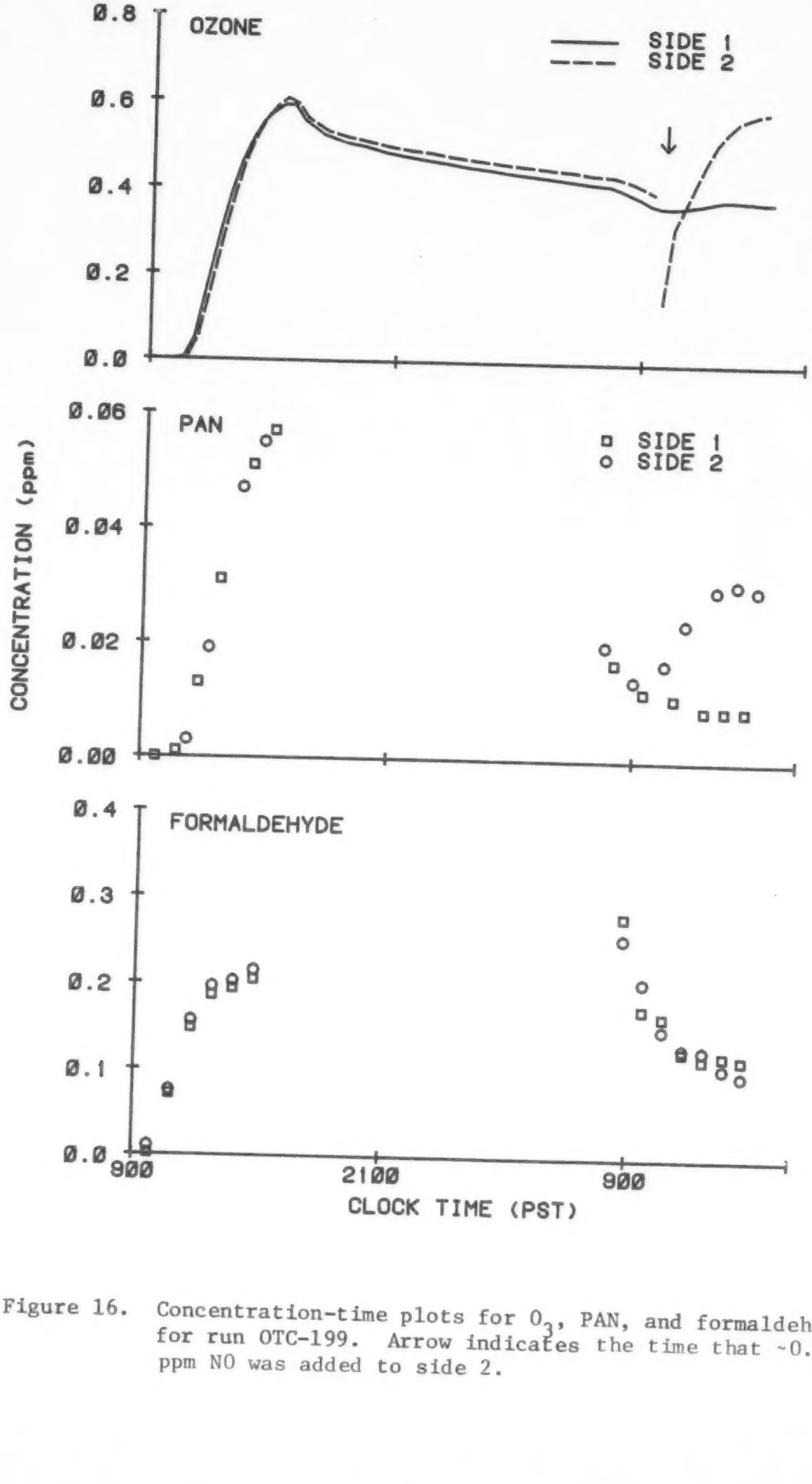

Figure 16. Concentration-time plots for O_3, PAN, and formaldehyde for run OTC-199. Arrow indicates the time that ~0.15 ppm NO was added to side 2.

and 4, resulting in substantial O_3 formation occurring on each day on that side. The resulting O_3 levels were comparable to, but somewhat higher than, the highest O_3 levels occurring on days 2 and 3 on the high NO_x side. Since the total amount of NO_x injected into the low initial NO_x side (~0.5 ppm) was less than the total NO_x injected into the high initial NO_x side (~0.8 ppm), this shows NO_x is much more efficient in promoting O_3 formation when relatively small amounts are injected each day, as opposed to all being initially present. This is as expected, since when O_3 formation occurs in runs with relatively high initial NO_x, the excess NO_x remaining at the end of the day tends to be consumed by reaction with O_3 during the night. If the initial NO_x is lower, such that most is consumed during the day, then the nighttime loss of NO_x and O_3 due to their mutual reaction is much less.

In the above discussion, we have focussed primarily on the ozone data, and the factors affecting them. However, as indicated in Section II.C, a number of other species were also measured. As a result of these experiments, the following general observations can be made concerning the behavior of some of the other important species under the conditions of these multi-day outdoor irradiations:

(1) In all of these experiments, the NO levels were generally negligible except during the initial part of the first day of the irradiation. This is because O_3 was usually present in excess, and in any case, there is no significant mechanism for reactive NO_x to be reduced back to NO after the initial NO has been oxidized.

(2) As indicated in Section II.C.3, NO_2 could not be monitored directly during these experiments; the quantity monitored (and reported as "NO_2-UNC" on the data sheets in Volume II and on the data sets in Volume III, or as "NO_x + Nitrates" or "Uncorrected NO_2" in this volume) was the total of all species which can be converted to NO by a heated molybdenum catalyst. This included NO_2, PAN, organic nitrates, and the fraction of HNO_3, if any, which made it to the catalyst without being adsorbed on the sample lines. In general, these "uncorrected NO_2" measurements usually reflected primarily NO_2 itself during the first day, exhibiting the typical profiles of rising to a maximum and then declining. During the nighttime, these measured levels declined, presumably reflecting the reaction of NO_2 with O_3. In some experiments, some NO_2 apparently remained in

this residual "uncorrected NO_2" mixture, since O_3 formation occurred during the next day without additional NO_x being added. However, in other runs this residual "uncorrected NO_2" contained negligible NO_2, as indicated by the lack of O_3 formation when irradiation resumed on the second and subsequent days. It is of interest that the level of this residual "uncorrected NO_2" consistently increased when the irradiations began on the subsequent days, and consistently declined in the dark, suggesting that some species, possibly HNO_3, was being desorbed from the wall by the light or the heat of the day, and re-adsorbed at night. This species cannot be NO_2, since frequently this rise in "uncorrected NO_2" was not accompanied by O_3 formation.

(3) PAN levels in general seemed to exhibit time-concentration profiles similar to those for O_3, with relatively more PAN being formed under conditions where O_3 formation was favored. PAN levels generally declined at night, though by variable amounts.

(4) Although, as discussed in Section II.C.2, the formaldehyde data obtained in this program were not very reliable, in most of the outdoor surrogate runs during the second phase of the program the HCHO data were sufficiently precise to allow an indication of its concentration-time behavior to be inferred. In general, HCHO levels increased throughout the first day, remained approximately constant at night, and declined throughout the second and subsequent days. In particular, there was no evidence in any of these experiments for significant formaldehyde adsorption onto the walls at night, followed by desorption during the subsequent day.

(5) The concentrations of all the surrogate components were also monitored throughout these experiments, and in most cases the data appear to be quite reliable and precise. As expected, the concentrations of these components decline during the day and remain essentially unchanged during the night. As with formaldehyde, the analytical data give no evidence for adsorption of these species at night and offgassing on subsequent mornings (but see the discussion in Section III.A.6). In general, the rate of decline of the surrogate components during the day, which reflect overall radical levels, did not have a strong dependence on the NO_x levels, unlike the rate of formation of O_3 (see, for example, the isooctane data plotted in Figure 15).

B. Indoor Chamber Studies

A total of 32 single and multi-day chamber experiments were carried out using the ~6400-ℓ indoor Teflon chamber during this program. These experiments included six multi-day surrogate-NO_x-air runs, one isobutene-NO_x-air run, two runs employing ambient air or ambient air + NO_x, three propene-NO_x-air conditioning or control runs, seven NO_x-air or NO_x-air + CO-NO_x-air irradiations, four acetaldehyde-air irradiations, one O_3 and O_3 + NO_x-air irradiation, one pure air irradiation, three O_3 dark decay determinations, and four NO_2 actinometry experiments. As with the outdoor runs, the indoor runs were carried out in two phases, the first around the beginning of 1983 and the second around the end of that same year. All of the multi-day surrogate runs were carried out during the first phase of the indoor chamber experiments; the second phase consisted primarily of an isobutene-NO_x-air irradiation (carried out at the request of the EPA's modeling contractors at Systems Applications, Inc.) and associated control runs. (The seven control runs carried out during the second phase were actually funded by another program; their results are included in this report since they also serve to characterize the conditions of the isobutene-NO_x-air run.) Detailed tabulations of the results of these experiments are given in Volume II of this report, and these data are given in computer-readable format in Volume III. In addition to the experimental measurements, these tabulations include notations made in the laboratory notebooks during the runs, and operator's comments indicating special circumstances concerning the data obtained, as for the outdoor experiments. Table 12 gives a chronological listing of these indoor runs, including a brief summary of the purpose, conditions, and major results of each experiment.

In the remainder of this section, the results of the various types of indoor chamber experiments are summarized and briefly discussed. A discussion of the light intensity measurements and spectral distribution of the lamps is given first, followed by a summary of the results of the various characterization runs. The results of the isobutene-NO_x-air run, the irradiations involving ambient air, and the multi-day surrogate runs are then briefly summarized and discussed.

Table 12. Summary of Indoor Chamber Experiments

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
				New reaction bag installed	
621	3/29/83	NO_x-air	Determine background reactivity of new bag	Initial NO = 0.25 ppm NO_2 = 0.07 ppm 2-hour run	$-d[NO]/dt = 0.23$ ppb min^{-1} Radical source = 0.07 ppb min^{-1}
622	3/29/83	Actinometry	Measure light intensity	NO_2 in N_2 in quartz tube	$k_1 = 0.305$ min^{-1}
623	3/30/83	Propene-NO_x-air	Conditioning	Initial NO = 0.23 ppm NO_2 = 0.23 ppm Propene = ~0.7 ppm (est.) 4-hour run	O_3 = 0.73 ppm at end of run
624	3/31/83	O_3 decay	Measure O_3 dark decay rate; bag conditioning	Initial O_3 = 2.18 ppm In chamber for 6.5 hours Dark run	Final O_3 = 2.02 ppm O_3 decay rate = 1.98×10^{-4} min^{-1}
625	4/1/83	NO_x-air + CO-NO_x-air	Determine reactivity of conditioned bag	Initial NO = 0.22 ppm NO_2 = 0.06 ppm 4-hour run ~50 ppm CO added at t = 2 hours	t = 1-2 hours (no CO): $-d[NO]/dt = 0.07$ ppb min^{-1} Radical source = 0.05 ppb min^{-1} t = 3-4 hours (with CO): $-d[NO]/dt = 0.43$ ppb min^{-1} Radical source = 0.07 ppb min^{-1}
626	4/4/83	Surrogate-NO_x-air	Measure reactivity of surrogate-NO_x-air run under multi-day conditions. Test effect of added NO to "spent" surrogate-NO_x-air mixture	Initial NO = 0.23 ppm NO_2 = 0.07 ppm Surrogate = 4.0 ppmC Surrogate components injected on previous day. Day 1: Lights on 0900-2100 PST Day 2: Lights on 0900-1500 PST ~0.77 ppm NO added 1000	Day 1: O_3 max at 0.62 (1900-2000 PST); O_3 fell from 0.56 to 0.51, little change in NO_x overnight Day 2: O_3 continued to fall after lights on. No O_3 formed following NO injection; excess NO fell slowly (0.33 ppm at 1015 PST to 0.25 ppm at 1500)

(continued)

Table 12 (continued) - 2

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
627	4/7/83	Acetaldehyde-air	Measure NO_x offgassing rate after 2-day run	Initial $CH_3CHO = 0.38$ ppm 6-hour run	PAN formation rate = 0.036 ppb min^{-1} Final $O_3 = 0.061$ ppm
628	4/8/83	NO_x-air + CO-NO_x-air	Determine chamber reactivity after 1 multi-day chamber run	Initial NO = 0.25 ppm $NO_2 = 0.08$ ppm 4-hour run 51.0 ppm CO added at t = 2 hours	t = 1-2 hours (no CO): $-d[NO]/dt = 0.04$ ppb min^{-1} Radical source = 0.06 ppb min^{-1} t = 3-4 hours (51 ppmC): $-d[NO]/dt = 0.47$ ppb min^{-1} Radical source = 0.06 ppb min^{-1}
629	4/8/73	Actinometry	Measure light intensity	NO_2 in N_2 in quartz tube	$k_1 = 0.276$ min^{-1}
630	4/11/83	Surrogate-NO_x-air	Repeat of run ITC-626 with less NO added on day 2 and less surrogate for lower reactivity	Initial NO = 0.23 ppm $NO_2 = 0.07$ ppm Surrogate = 1.94 ppmC Day 1: Lights on 0900-2100 PST Day 2: Lights on 0900-2100 PST 0.25 ppm NO injected at 1200 PST Day 3: 0900-1030 PST, 35% lights; 1030-2100 PST, 70% lights	Day 1: Final $O_3 = 0.28$ ppm (not max) O_3 fell to 0.17 ppm, NO_2 (uncorr) from 0.19 to 0.08 ppm overnight Day 2: O_3 rose slowly to 0.21 ppm by 1200 PST. After NO injection, 0.14 ppm O_3 formed in 9 hours (not max). O_3 fell to 0.04 ppm; NO_2 (uncorr) from 0.18 to 0.04 ppm overnight Day 3: O_3 rose from 0.04 to 0.27 ppm in 12 hours. NO_2 (uncorr) rose to 0.06 ppm
631	4/18/83	Surrogate-NO_x-air	Repeat of run ITC-630 with less surrogate	Initial NO = 0.24 ppm $NO_2 = 0.09$ ppm Surrogate = 1.04 ppmC Days 1,2: Lights on 0900-2100 PST Day 3: Lights on at 0900 PST, left on for 21.75 hours	Day 1: Negligible O_3 formation; most NO consumed. No dark reaction overnight Day 2: Final $O_3 = 0.17$ ppm (not max). O_3 fell to 0.08 ppm, NO_2 (uncorr) from 0.13 to 0.03 ppm overnight Day 3: O_3 rose to a maximum of 0.25 ppm in ~16 hours of irradiation, then declined to 0.21 ppm at end of run. NO_2 (uncorr) rose to 0.05 ppm

(continued)

Table 12 (continued) - 3

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
632	4/22/83	Acetaldehyde-air	Measure NO_x offgassing rate after series of multi-day runs, with chamber not flushed	Chamber not flushed after previous run; flattened and refilled Initial CH_3CHO = 0.63 ppm 6-hour run	PAN formation rate = 0.03 ppb min^{-1} Final O_3 = 0.051 ppm
633	4/25/83	Surrogate-NO_x-air	Measure effect of increasing both NO_x and surrogate	Initial NO = 0.46 ppm NO_2 = 0.18 ppm Surrogate = 3.97 ppmC Days 1,2: Lights on 0900-2100 PST Day 3: Lights on 0900-1600 PST	Day 1: Final O_3 = 0.23 ppm (not max) O_3 fell to 0.03 ppm, NO_2 (uncorr) from 0.43 to 0.16 ppm overnight Day 2: Final O_3 = 0.32 ppm (still rising slowly) O_3 fell to 0.26 ppm, NO_2 (uncorr) fell from 0.08 to 0.05 ppm overnight Day 3: O_3 rose slowly to 0.27 ppm at 1600
634	5/2/83	NO_x-air + CO-NO_x-air	Monitor reactivity of chamber at the NO_x levels of run ITC-633	Initial NO = 0.46 ppm NO_2 = 0.14 ppm 4-hour run 52 ppm CO added at t = 2 hours	t = 1-2 hours (no CO): $-d[NO]/dt$ = 0.08 ppb min^{-1} Radical source = 0.07 ppb min^{-1} t = 3-4 hours (52 ppmC CO): $-d[NO]/dt$ = 0.29 ppb min^{-1} Radical source = 0.05 ppb min^{-1}
635	5/2/83	Surrogate-NO_x-air	Repeat of run ITC-633 with higher NO_x	Initial NO = 0.90 ppm NO_2 = 0.30 ppm Surrogate = 4.01 ppmC Day 1: Lights on 0900-2100 PST Day 2: Lights on at 0900 PST and left on Day 3: End of run at 0830 PST	Day 1: No O_3 formed. Final NO = 0.47 ppm. Slow oxidation of NO to NO_2 overnight Day 2: Negligible O_3 formation in 23.5 hours. NO fell from 0.41 to 0.15 ppm
636	5/5/83	Acetaldehyde-air	Monitor NO_x offgassing rate of chamber	Initial CH_3CHO = 0.54 ppm 6-hour run	PAN formation rate = 0.03 ppb min^{-1} Final O_3 = 0.046 ppm
637	5/9/83	Surrogate-NO_x-air	Repeat of run ITC-626. Determine effect of multiple NO injections on subsequent days	Initial NO = 0.24 ppm NO_2 = 0.07 ppm Surrogate = 3.94 ppmC	Day 1: O_3 maximum = 0.617 ppm at 1730-1830; dropped to 0.60 at 2100. O_3 fell to 0.50 ppm and NO_2 (uncorr) from 0.17 to 0.09 ppm overnight

(continued)

Table 12 (continued) - 4

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
637 (continued)				Day 1: Lights on 0900-2100 PST Day 2: Lights on 0900-2100 PST 0.19 ppm NO injected at 1000 PST Day 3: Lights on 0900-2100 PST 0.19 ppm NO injected at 1000 PST Day 4: Lights on 0900-2330 PST 0.29 ppm NO injected at 1000 PST	Day 2: O_3 fell to 0.46 by 1000 PST. After NO added, O_3 rose from 0.26 to 0.58 ppm at 2100 PST; NO_x fell throughout day. O_3 fell to 0.44 ppm, NO_2 (uncorr) from 0.10 to 0.06 ppm overnight Day 3: O_3 essentially constant before NO injected. After injection, O_3 rose from 0.24 to 0.54 at 2030 PST. O_3 fell to 0.38, NO_2 (uncorr) fell from 0.08 to 0.06 overnight Day 4: O_3 fell to 0.36 by 1000 PST. After NO injection O_3 rose from 0.11 ppm to a maximum of 0.33 ppm at 1830-1945 PST, then dropped to 0.29 ppm at 2330 PST. NO_x dropped throughout day
638	5/14/83	NO_x-air + CO-NO_x-air	Monitor reactivity of chamber	Initial NO = 0.24 ppm NO_2 = 0.08 ppm 4-hour run 50 ppm CO added at t = 2 hours	t = 1-2 hours (no CO): -d[NO]/dt = 0.05 ppb min^{-1} Radical source = 0.06 ppb min^{-1} t = 3-4 hours (50 ppm CO): -d[NO]/dt = 0.42 ppb min^{-1} Radical source = 0.07 ppb min^{-1}
639	5/17/83	Acetaldehyde-air	Monitor NO_x offgassing rate	Initial CH_3CHO = 0.35 ppm 6-hour run	PAN formation rate = 0.03 ppb min^{-1} Final O_3 = 0.046 ppm
640	5/18/83	O_3, O_3 + NO_x-air	Monitor O_3 consumption rate upon irradiation in the absence of reactive organics and NO_x; monitor O_3 consumption in the presence of NO_x upon irradiation and in the dark	Initial O_3 = 0.53 ppm Lights on for 4.25 hours Then monitored for additional 3 hours in the dark 0.21 ppm NO added at t = 1 hour	O_3 fell from 0.533 to 0.516 ppm in first hour (no NO_x). O_3 consumption rate ≅ 5.4 x 10^{-4} min^{-1}. O_3 fell from 0.299 to 0.243 in 3 hours in the presence of ~0.21 ppm NO_2. Consumption rate ≅ 11.5 x 10^{-4} min^{-1}. In the dark, O_3 fell from 0.243 to 0.142 ppm, NO_2 from 0.199 to 0.041 ppm in 3 hours
641	5/18/83	O_3 dark decay	Monitor O_3 dark decay rate	Initial O_3 = 0.47 ppm. O_3 monitored for 18.42 hours	O_3 decay rate ≅ 0.6 x 10^{-4} min^{-1}

(continued)

Table 12 (continued) - 5

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
642	5/20/83	Pure air	Monitor O_3 formation upon irradiation of purified air in this chamber	No injections 6.25-hour run	Final O_3 = 0.046 ppm NO_x (uncorr) rose from 15 to 24 ppb
643	5/24/83	Polluted air	Monitor reactivity upon irradiation of polluted evening air	Day 1: Chamber flushed continuously with ambient air from 1331 to 1626 PST on 5/24. 45 % RH. Ambient O_3 $\gtrsim$0.14 ppm. No irradiation Day 2: Lights on 0915-1515 PST	Day 2: O_3 dropped from 0.094 to 0.079 ppm in the dark. O_3 rose to 0.14 ppm upon irradiation for 6 hours. NO_2 (uncorr) rose from 31 ppb to 43 ppb. No capillary GC data due to calibration problems
644	5/25/83	Polluted air + NO_x	Monitor reactivity upon irradiation of polluted evening air in the presence of added NO_x	Day 1: Chamber flushed continuously with ambient air from 1530-1645 PST. 45% RH. Day 2: 0.04 ppm NO added at 0915 PST and lights on. 6-hour irradiation	Day 2: O_3 ≅ 0.072 ppm prior to NO injection. After NO added and irradiation begun, O_3 rose from 0.025 to 0.097 ppm after end of the run. NO_2 (uncorr) dropped slowly from 55 to 49 ppb. No capillary GC data due to calibration problems
				46 Runs Carried out for Other Programs. New Reaction Bag Installed	
690[b]	11/23/83	"Dummy" Propene-NO_x-air	Chamber conditioning	Initial NO = 0.21 ppm NO_2 = 0.23 ppm Propene = 0.76 ppm 5-hour run	No data taken Conditioning run Ozone formed
691[b]	11/28/83	NO_2 actinometry	Determine light intensity	Quartz tube technique - NO_2 in N_2	k_1 = 0.286 min^{-1}; same as in the previous determination
692[b]	11/28/83	NO_x-air	Monitor chamber effects	Initial NO = 0.39 ppm NO_2 = 0.11 ppm Propene/n-butane tracers 2-hour run	Radical input rate = 0.15 ppm min^{-1} NO oxidation rate = 0.12 ppb min^{-1} (in the normal-high range for this chamber)

(continued)

Table 12 (continued) - 6

ITC Run No.	Date Started	Description	Purpose	Initial Concentrations[a] and Experimental Operations	Major Results and Remarks
693[b]	11/29/83	Propene-NO_x-air	Standard control run for chamber performance	Initial NO = 0.38 ppm NO_2 = 0.11 ppm Propene = 1.10 ppm 6-hour run	Final O_3 = 0.78 ppm, in reasonable agreement with model predictions
694	11/30/83	Isobutene-NO_x-air	Test kinetic model for this surrogate component	Initial NO = 0.40 ppm NO_2 = 0.11 ppm Isobutene = 1.14 ppm 6-hour run	Maximum O_3 = 0.90 ppm in 5.25 hours
695[b]	12/1/83	NO_x-air	Monitor chamber effects	Initial NO = 0.40 ppm NO_2 = 0.10 ppm Propene/n-butane tracers 2-hour run	Radical input rate = 0.13 ppb min^{-1} NO oxidation rate = 0.23 ppb min^{-1}
696[b]	12/1/83	NO_2 actinometry	Determine light intensity	Quartz tube technique - NO_2 in N_2	k_1 = 0.286 min^{-1}, exactly the same as in the previous two determinations
697[b]	12/1/83	Ozone decay	Determine O_3 dark decay rates	Initial O_3 = 1.14 ppm; left in chamber 15.6 hours (overnight). Dark run	Final O_3 = 0.96 ppm; O_3 decay rate = 1.1% $hour^{-1}$

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[a] Unless otherwise noted, ~50% RH pure air used, T = 32 ± 1 C, and 70% lights employed.

[b] Carried out under funding for another program. Included in the list because these runs serve as characterization runs for the isobutene-NO_x-air experiment.

1. Light Intensity and Spectral Distribution

In order for the results of these runs to be useful for model testing purposes, both the intensity and the spectral distribution of the photolyzing light must be known. As discussed in Section II.C.4, the absolute light intensity, which was constant during all these irradiations, was monitored periodically by NO_2 actinometry using the quartz tube technique of Zafonte et al. (1977). The NO_2 photolysis rates measured at 70% of the maximum light intensity (the intensity employed in all experiments reported here) with the set of lamps employed during these experiments are plotted against ITC run number in Figure 17. This figure includes runs conducted before, during, and after the experiments carried out in this program, and the arrows in the figure indicate the first and last ITC runs of this program. The lines on the figure indicate least squares regressions or averages of the data for the periods indicated. It can be seen that although the light intensity fell relatively rapidly when the lamps were new, and had an unexpected ~10% increase shortly after the series of experiments for this program were completed, it appeared to be relatively constant during the period of the runs reported here (runs ITC-621 through 644), and indicated that an NO_2 photolysis rate of 0.30 min^{-1} was appropriate for all irradiations given in this report, with an estimated uncertainty of ~10%.

In order to calculate rates of the other photolysis reactions, the relative spectral distribution must also be known. The spectral distribution of the blacklights in the indoor Teflon chamber was measured immediately following the first series of runs, and the relative light intensities (in terms of photons per unit area per unit time) at selected wavelengths are given in Table 13. The wavelengths in Table 13 were chosen such that the true light intensity spectrum can be well approximated by a series of straight lines between each of the tabulated points for the purpose of computing the photolysis rates. It should be noted that the blacklights employed are significantly less intense in the λ = 300-330 nm and the $\lambda \geq 400$ nm regions than sunlight (Peterson 1976), and thus it is not appropriate to use photolysis rates calculated for the atmosphere when using these data for model testing.

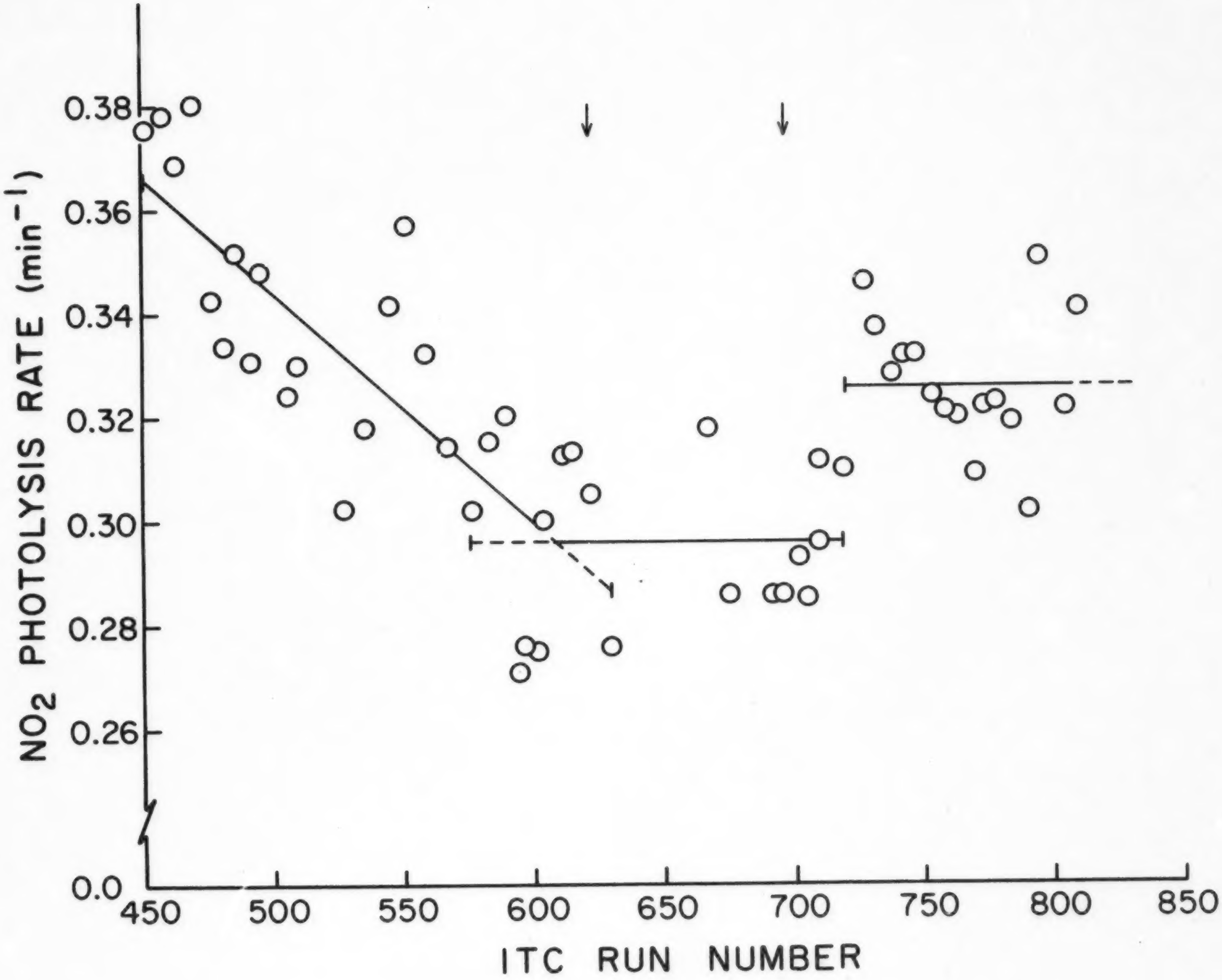


Figure 17. Plot of NO_2 photolysis rates measured in the SAPRC indoor Teflon chamber against run number. Lines shown are linear least squares regressions or averages of the data over the indicated ranges.

Table 13. Relative Spectral Distribution for the Blacklights in the SAPRC 6400-ℓ Indoor Teflon Chamber[a]

Wavelength (nm)	Intensity[b]	Wavelength (nm)	Intensity[b]	Wavelength (nm)	Intensity[b]
295.7	0.0	347.8	0.952	405.0	0.258
296.7	0.0019	350.0	0.972	406.0	0.264
298.0	0.0024	351.7	0.990	406.7	0.251
300.7	0.0018	353.7	1.00	408.7	0.0596
302.1	0.0043	356.7	0.982	412.0	0.0387
304.3	0.0058	360.0	0.925	416.7	0.0348
306.3	0.0057	363.3	0.829	423.3	0.0298
310.0	0.0140	364.3	0.859	430.0	0.0227
313.0	0.0728	364.7	0.869	434.3	0.0217
313.7	0.0846	365.5	0.870	436.1	0.641
315.0	0.0879	366.9	0.835	436.7	0.709
315.3	0.0856	368.5	0.685	437.3	0.712
316.7	0.0581	370.0	0.639	438.1	0.651
317.3	0.0564	376.7	0.442	439.7	0.0169
318.7	0.0858	383.3	0.261	443.3	0.0140
323.3	0.1495	390.0	0.1423	450.0	0.0081
330.0	0.331	396.7	0.0885	460.0	0.0
336.7	0.563	393.0	0.0535		
343.3	0.851	404.3	0.223		

[a] As measured on June 30, 1983

[b] Intensity in terms of photons per unit area per unit time, normalized so the maximum intensity = 1.0 units.

2. Characterization Runs

The results of the NO_x-air irradiations carried out in the indoor chamber during this program are summarized in Table 14. The purpose of this type of experiment and methods of data analysis were discussed previously in Section III.A.2. It can be seen that somewhat different results were obtained in the two different reaction bags employed. In the case of the bag employed during the first series (when all of the multi-day surrogate-NO_x-air irradiations and ambient air experiments were carried out), it can be seen that, other than the anomalously high NO oxidation rate observed in run ITC-621, reasonably consistent results were obtained in the replicate runs, indicating no significant change in chamber characteristics during this series of experiments. The high NO oxidation rate in run ITC-621 can be attributed to the fact that it was obtained in a new, unconditioned bag, since new Teflon material has been

Table 14. Results of NO_x-Air and CO-NO_x-Air Irradiations in the SAPRC Indoor Teflon Chamber

ITC Run No.		621	625	628	634	638	692[a]	695[a]
Initial NO	(ppm)	0.25	0.22	0.25	0.46	0.24	0.39	0.40
NO_2	(ppm)	0.07	0.06	0.08	0.14	0.08	0.11	0.10
Average T	(C)	26±2	29±2	26±2	29±2	28±1	27±2	28±1
For CO = 1-2 ppm[b]								
Avg. [NO_2]	(ppm)	0.08	0.07	0.08	0.13	0.08	0.12	0.11
10^{-6} x [OH]	(cm^{-3})	1.37	1.25	1.05	0.78	1.18	1.82	1.79
Rad. input rate	(ppb min^{-1})	0.07	0.05	0.06	0.07	0.06	0.15	0.13
-d[NO]/dt	(ppb min^{-1})	0.23	0.07	0.04	0.08	0.05	0.12	0.23
For CO ≅ 50 ppm[c]								
Avg. [NO_2]	(ppm)	-	0.12	0.13	0.16	0.13	-	-
10^{-6} x [OH]	(cm^{-3})	-	0.93	0.65	0.44	0.82	-	-
Rad. input rate	(ppb min^{-1})	-	0.07	0.06	0.05	0.07	-	-
-d[NO]/dt	(ppb min^{-1})	-	0.43	0.47	0.29	0.42	-	-

[a] Second series: different reaction bag used.
[b] Data from second hour of the irradiation used.
[c] Data from the fourth hour of the irradiation used.

shown to exhibit significant contamination by CO and hydrocarbons, which is reduced upon irradiation and flushing (Kelly 1981). Otherwise, the results of these experiments carried out during the first (and major) phase of the indoor chamber experiments were within the range previously observed for this type of chamber (Carter et al. 1982, Pitts et al. 1983).

For the reactor employed during the second phase of indoor experiments (i.e., for the isobutene-NO_x-air experiment), consistently higher radical input and NO oxidation rates were observed. (Subsequent experiments carried out for another program employing that reactor gave results totally consistent with results of runs ITC-692 and 695). The reason for the higher reactivity of this bag is unknown, but the data in Table 14 indicate clearly that different Teflon bag reactors, both of which were constructed of the same type of FEP Teflon material, can have different reactivity characteristics, and this must be taken into account when using these experiments for model testing.

For the purposes of obtaining an alternate measurement of the radical input rates (see Section III.A.2), some NO_x-air irradiations were carried out in the presence of ~50 ppm of added CO. As expected, the addition of CO during the NO_x-air irradiations caused the NO oxidation rates to increase. The average OH radical levels were lower during the portion of the experiment when the CO was present, though this may be due to higher average NO_2 levels, and not necessarily to any direct effect of CO on radical levels.

In order to monitor NO_x offgassing rates (see the discussion in Section III.A.1), four acetaldehyde-air irradiations were conducted at various times during the first series of indoor runs, and the results are summarized in Table 15. It can be seen that there is no evidence for an increase in NO_x offgassing rates with the life of the reaction bag. For modeling puposes, it appears that a constant NO_x offgassing rate of 0.03 ppb min^{-1} is appropriate for all these runs in the absence of NO_x, though these runs do not indicate whether NO_x offgassing also occurs when NO_x is already present. The O_3 yield after six hours averaged ~50 ppb, which was not greatly different from the six-hour O_3 yield of 41 ppb in the pure air irradiation (run ITC-642).

Two O_3 dark decay experiments were also carried out during the first series of experiments and one during the second. The first O_3 decay run carried out during the first series when the bag employed was newly conditioned (run ITC-624) gave an O_3 decay rate of $\sim 2 \times 10^{-4}$ min^{-1}, which

Table 15. Results of Acetaldehyde-Air Irradiations in the SAPRC Indoor Teflon Chamber

ITC Run No.	Initial CH_3CHO (ppm)	Avg. T (C)	Ozone (ppb) 6-hour	PAN Yield (ppb)		PAN Formation Rate (ppb min^{-1})	
				3-hour	6-hour	0-3 hour	3-6 hour
627	0.38	28±2	61	8	13	0.04	0.03
632[a]	0.63	29±1	51	6	9	0.03	0.02
636	0.54	29±1	46	7	11	0.04	0.02
639	0.35	29±1	46	5	10	0.03	0.03

[a] Chamber emptied and refilled after previous (surrogate-NO_x-air) run; not flushed.

was essentially the same as the result of the O_3 decay experiments carried out at the end of the second series (run ITC-697), after the reactor had been employed for the isobutene-NO_x-air irradiation and associated conditioning and control runs. However, run ITC-641, which was carried out near the end of the first series, gave an O_3 decay of only 0.6×10^{-4} min^{-1}. It is not clear whether this decrease reflects a conditioning effect of the surrogate-NO_x-air runs on the bag, or merely day-to-day variability. In any case, even the higher rate is relatively low, representing only a ~7% loss in O_3 in six hours, so this should not represent a significant uncertainty in model simulations of these runs.

In addition to the above, a pure air irradiation (run ITC-642) and an O_3 and O_3 + NO_x-air irradiation (run ITC-640) were carried out for control purposes. As expected, there was a gradual formation of O_3 in the pure air irradiation, but in addition there was a slight increase in the levels of species which are converted to NO by the catalyst in the NO-NO_x analyzer, indicating some offgassing of these species adsorbed on the walls (see Section II.C.3 and III.A.8). The results of this run can be compared with the results of the ambient air irradiation, which is discussed below in III.B.4.

The O_3 and O_3 + NO_x-air irradiation (run ITC-640) was carried out in order to simulate the subsequent days of multi-day surrogate experiments, with the surrogate and its organic reaction products absent. When irradiated by itself, O_3 decayed at a rate of $\sim 5 \times 10^{-4}$ min^{-1}, which was within the range observed in the surrogate irradiations after the NO_x was consumed. When irradiated in the presence of ~0.2 ppm NO_2, the O_3 consumption rate increased by a factor of ~2. This contrasted with the results of the surrogate runs, where the presence of NO_x caused O_3 to be formed, clearly indicating that, as expected, the rapid formation of O_3 following the addition of NO_x in subsequent days of the surrogate-NO_x-air runs was due to the presence of the surrogate and its reaction products, and was not a chamber effect. When the lights were turned off, both O_3 and NO_2 decreased, as was the case during the "night" in the multi-day surrogate irradiations. The ratio of NO_2 to ozone consumed was ~1.6, which can be compared to the expected ratio of 2 due to the reactions

$$NO_2 + O_3 \rightarrow NO_3 + O_2$$

$$NO_3 + NO_2 \overset{M}{\rightleftarrows} N_2O_5$$

$$N_2O_5 + H_2O \xrightarrow{\text{wall}} 2HNO_3$$

though it should be noted that if the HNO_3 formed was interfering with the NO_x analyses, then a lower ratio would be observed. (Indeed, the stoichiometry of the dark O_3 and NO_2 consumption during the surrogate irradiations cannot be determined, due to the presence of uncharacterized interferences in the NO_2 analyses). However, in single-day indoor chamber irradiations (such as run ITC-640), HNO_3 interferences were generally not a problem, suggesting that this ratio of 1.6 may be valid. This indicates that additional reactions may be involved with the dark O_3 and NO_2 consumption process characteristic of these multi-day runs.

Finally, at various times during the indoor chamber experiments, propene-NO_x-air irradiations were carried out. These were carried out either to condition the reaction bags or, in the case of run ITC-693, for control purposes for model testing. Thus propene-NO_x-air models have been developed which generally give good results in simulating data obtained in other chambers (Carter et al. 1979, Atkinson et al. 1982), and it was important to assure that the models can also simulate data in this chamber for this relatively well-characterized chemical system. Preliminary model calculations carried out at our laboratories (Carter, unpublished results) indicate that the data for run ITC-693 are reasonably consistent with predictions based on the mechanism of Atkinson and Lloyd (1984).

3. Isobutene-NO_x-Air Irradiations

As indicated above, one isobutene-NO_x-air irradiation was carried out for the purpose of testing computer models for this compound, which was included in the surrogate to provide for rapid formaldehyde formation. Concentration-time plots for the reactants and the major products observed are shown in Figure 18. It can be seen that, as expected, isobutene was rapidly consumed, and formaldehyde and acetone were formed as the major products. These species are expected to be formed following the reactions of isobutene with OH radicals:

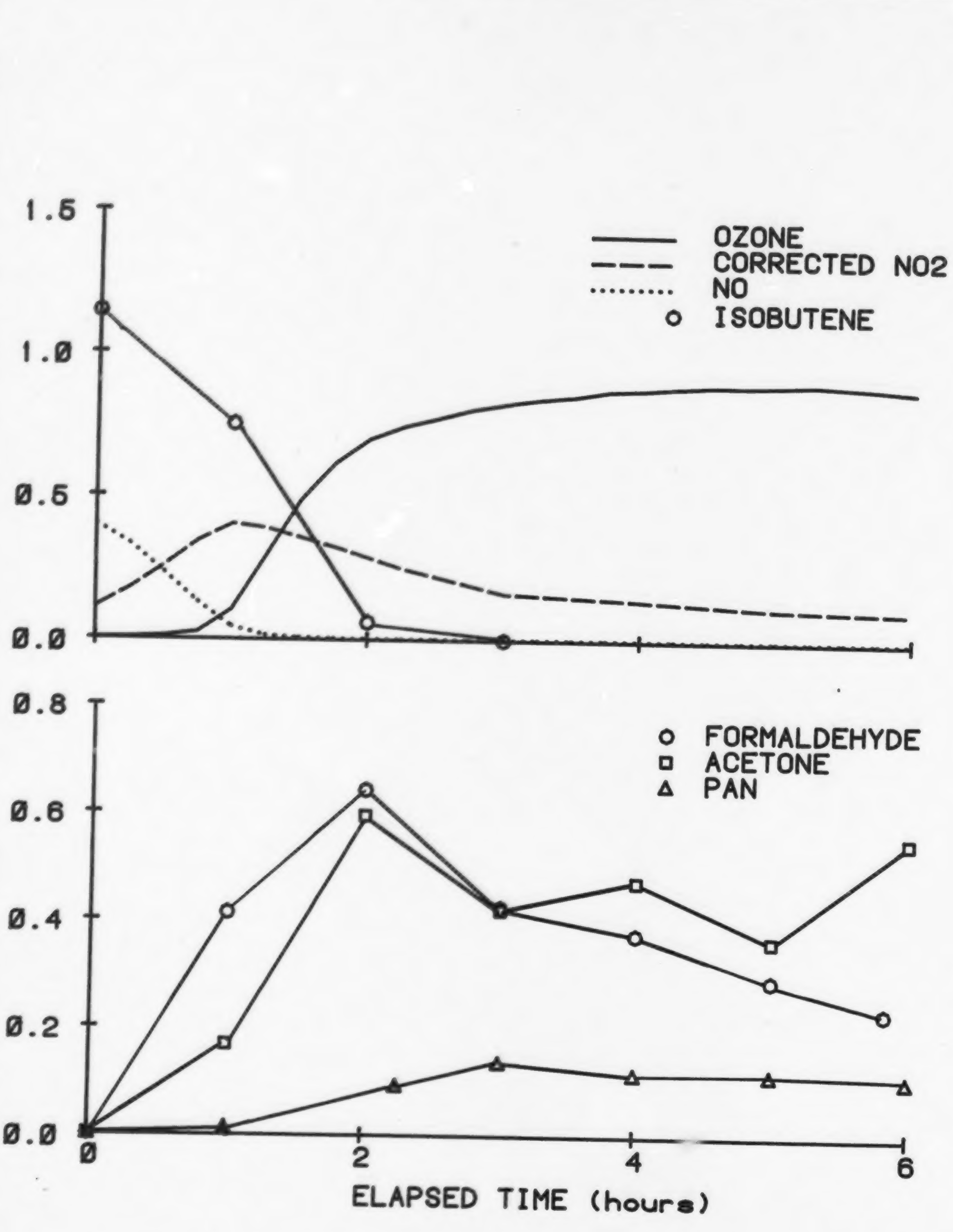
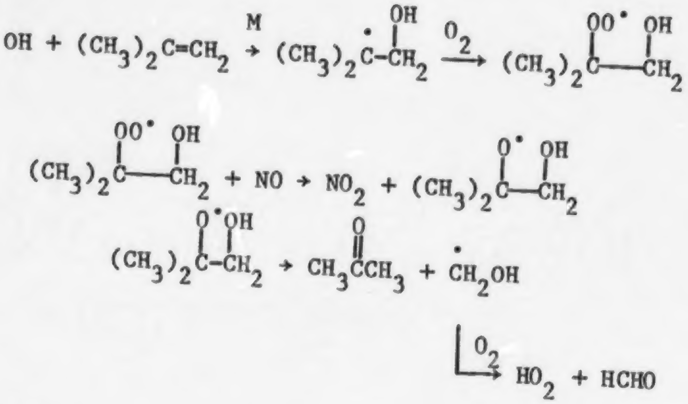


Figure 18. Concentration-time plots for major products and reactants observed in isobutene-NO_x-air run ITC-694. The NO_2 data shown have been corrected for an assumed 100% interference by PAN.

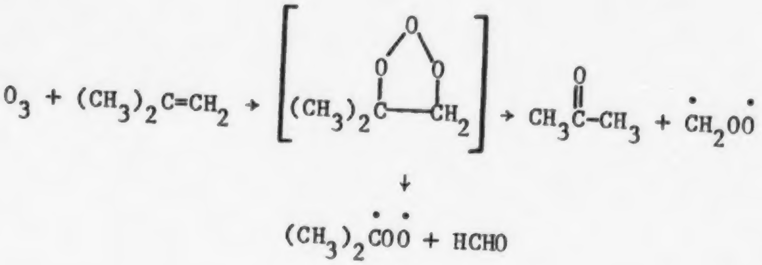


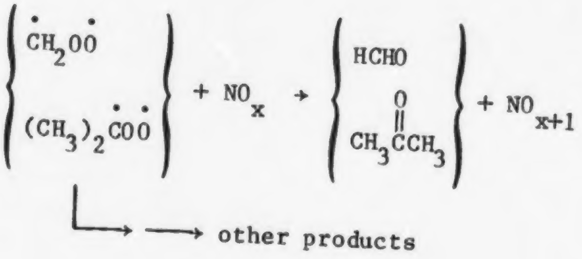
$$OH + (CH_3)_2C{=}CH_2 \xrightarrow{M} (CH_3)_2\overset{\bullet}{C}{-}\overset{OH}{CH_2} \xrightarrow{O_2} (CH_3)_2\overset{OO^\bullet}{C}{-}\overset{OH}{CH_2}$$

$$(CH_3)_2\overset{OO^\bullet}{C}{-}\overset{OH}{CH_2} + NO \rightarrow NO_2 + (CH_3)_2\overset{O^\bullet}{C}{-}\overset{OH}{CH_2}$$

$$(CH_3)_2\overset{O^\bullet}{C}{-}\overset{OH}{CH_2} \rightarrow CH_3\overset{O}{\overset{\|}{C}}CH_3 + \overset{\bullet}{C}H_2OH \xrightarrow{O_2} HO_2 + HCHO$$

and also, at least to some extent, following the reaction of isobutene with O_3:





$$\left\{\begin{matrix}\overset{\bullet}{C}H_2O\overset{\bullet}{O} \\ (CH_3)_2\overset{\bullet}{C}O\overset{\bullet}{O}\end{matrix}\right\} + NO_x \rightarrow \left\{\begin{matrix}HCHO \\ CH_3\overset{O}{\overset{\|}{C}}CH_3\end{matrix}\right\} + NO_{x+1}$$

$$\longrightarrow \text{other products}$$

PAN was also observed to be formed in significant yields in this system (though not as much as was formed from propene); it could be formed as a secondary product from the reactions of acetone, or more probably via additional routes following the reaction of O_3 with isobutene. Model calculations should give a more clear indication as to the most likely source of this PAN.

4. Ambient Air Irradiations

Two irradiations of moderately polluted Riverside evening air were conducted in the indoor Teflon chamber, one (run ITC-643) in which no additional species were added, and the other (run ITC-644) in which ~0.04 ppm of NO was added immediately prior to the irradiation. In both cases, the chamber was thoroughly flushed with ambient air for a period ending at ~1630-1645 PST, and the contents were then held in the dark until the irradiation commenced the following morning. An attempt was made to monitor the levels of as many of the organic pollutants as possible but experimental problems due to the effects of humidity on chromatographic retention times resulted in no quantitative capillary column gas chromatographic data being obtained. However, the levels of organics in these runs appeared to be relatively low, certainly much lower than the levels employed in the surrogate-NO_x-air irradiations. This does not, however, rule out the possible presence of significant levels of oxygenated pollutants and other species to which the analytical techniques employed were not sensitive.

The first experiment (run ITC-643) consisted of irradiation of polluted air without any additional reactants injected. However, despite the presence of pollutants (as indicated by an O_3 level of 160 ppb at the time the air was introduced into the chamber), the results of this run without added NO resembled those for the pure air irradiation discussed above. The O_3 increased at a rate of ~10 ppb hr^{-1} (compared to ~7 ppb hr^{-1} for the pure air run), and the species converted to NO by the converter on the NO_x-analyzer also increased slightly. Thus the presence of pollutants from the ambient air did not appear to have a significant effect in this experiment.

The other ambient air run (ITC-644) employed air with similar levels of pollution (based on measured initial O_3 values), but in this case a small amount of NO was added at the beginning of the irradiation. The amount of NO added was not sufficient to consume all the ~70 ppb of initially present O_3, and thus the NO was all converted to NO_2. The results of this O_3 + NO_2 + polluted air irradiation were intermediate between the results of the O_3 + NO_2 + pure air irradiation (where O_3 declined) and the subsequent days of surrogate-NO_x-air irradiations when NO was added (where O_3 rapidly increased). In this run, the O_3 increased at a very gradual rate of ~12 ppb hr^{-1}. Thus the pollutants in the Riverside air have some effect on the O_3 + NO_2 system, though not nearly as much as the partially reacted surrogate components at the levels employed in the surrogate-NO_x-air experiments carried out in this program.

5. Surrogate-NO_x-Air Irradiations

The conditions and selected results of the six multi-day surrogate-NO_x-air irradiations carried out in the indoor Teflon chamber for this program are summarized in Table 16. As discussed previously in Section II.B.2, no attempt was made to simulate the diurnal variation of light intensity for these multi-day runs; instead, 70% of the lights ($k_1 \cong 0.29$, see Section III.B.1) were turned on for 12 hours to simulate daytime conditions. This was carried out at the request of the EPA's modeling contractors at Systems Applications, Inc., in order to simplify the modeling of these runs. All runs were carried out at 50% RH, which was the case for the control runs as well. In most runs, if no O_3 formation was occurring on the second or subsequent day of the irradiation, presumably due to the fact that all the NO_x had reacted, variable amounts of NO were added to simulate injection of NO into an aged air mass, and to allow additional O_3 formation to continue. In some runs, if O_3 was still increasing on the 12th hour of the final day of irradiation, the irradiation was allowed to continue for longer than 12 hours so the maximum O_3 level could be determined.

The results of these runs were qualitatively similar to those for the outdoor chamber multi-day surrogate runs discussed previously in Section III.A.8. For example, Figure 19 compares the results of experiments with differing initial NO_x levels, and Figure 20 compares results of experiments where the initial surrogate concentrations were varied. (In both cases data taken after subsequent NO injections are not shown.) It can be seen that increasing the initial NO_x concentration decreased the O_3 formation on the first day, but resulted in greater O_3 formation on the second day, unless, as was the case for run ITC-635, the initial NO_x concentration was so high that it suppressed O_3 formation on the second day as well. The results shown in Figure 20 indicate that while decreasing the initial hydrocarbon concentration significantly decreased the O_3 formation on the first day, it also increased the amount of ozone formed on subsequent days, presumably because more of the initial NO_x remained on subsequent days of the irradiation. Similar results were obtained in

Table 16. Results of Multi-Day Surrogate-NO_x-Air Irradiations in the SAPRC Indoor Teflon Chamber

ITC Run Number	626	630	631	633	635	637	
Initial							
NO (ppm)	0.23	0.23	0.24	0.46	0.90	0.26	
NO_2 (ppm)	0.07	0.07	0.09	0.18	0.30	0.07	
Surrogate (ppmC)	4.0	1.94	1.04	3.97	4.01	3.94	
Day 1							
Final							
O_3 (ppm)	0.56	0.28	0.04	0.23	~0	0.60	
NO_x + nitrates (ppm)	0.12	0.19	0.26	0.43	1.06	0.17	
PAN (ppb)	116	27	2	34	1	100	
Average							
T (light) (C)	27±1	29±1	29±1	28±1	29±1	29±1	
(dark) (C)	19±2	22±1	23±1	23±1	23±1	23±1	
Day 2							
Initial							
O_3 (ppm)	0.51	0.17	~0	0.03	~0	0.50	
NO_x + nitrates (ppm)	0.08	0.08	0.25	0.16	1.02	0.09	
PAN (ppb)	56	24	1	42	0	30	
NO injected (ppm)	0.77	0.25	-	-	-	0.19	
Time NO injected[a] (hr)	1	3	-	-	-	1	
Final							
O_3 (ppm)	~0	0.14	0.17	0.32	0.02	0.58	
NO_x + nitrates (ppm)	0.85	0.20	0.13	0.08	0.56	0.10	
PAN (ppb)	~0	8	8	33	2	64	
HCHO (ppm)	0.03	0.01	~0	~0	-	0.01	
Average T (light) (C)	26±2	28±1	29±1	28±1	28±1	29±1	
(dark) (C)	-	22±1	23±1	23±1	-	23±1	
Duration of irrad. (hr)	6	12	12	12	23.5	12	
Days 3-4							
Initial						Day 3	Day 4
O_3 (ppm)	-	0.04	0.08	0.26	-	0.44	0.38
NO_x + nitrates (ppm)		0.05	0.03	0.05	-	0.06	0.05
PAN (ppb)		12	10	14	-	19	13
NO injected (ppm)	-	-	-	-	-	0.19	0.29
Time NO injected[a] (hr)	-	-	-	-	-	1	1
Final							
O_3 (ppm)	-	0.27	0.21	0.27	-	0.54	0.29
NO_x + nitrates (ppm)	-	0.06	0.05	0.06	-	0.08	0.08
PAN (ppb)	-	23	16	20	-	44	30
Average T (light) (C)	-	28±1	29±1	29±1	-	30±1	28±1
(dark) (C)	-	-	-	-	-	23±1	-
Duration of irrad. (hr)	-	12	21.75	7	-	12	14.5

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[a] Time after lights on for that day.

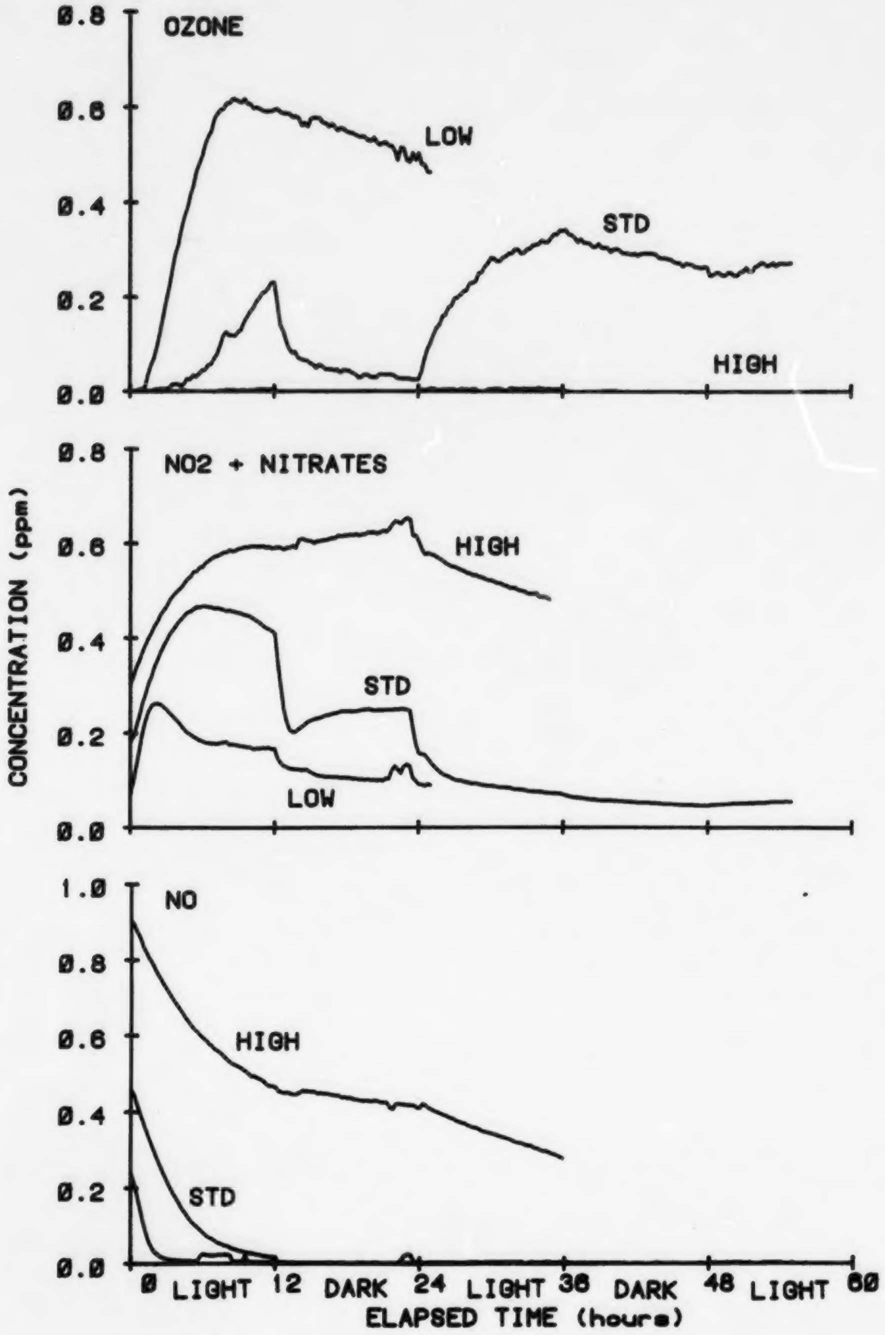

Figure 19. Concentration-time plots for O_3, uncorrected NO_2, and NO observed in indoor Teflon chamber runs ITC-633, 635, and 637. "Low," "STD," and "high" refer to runs with ~0.3, ~0.6 and 1.2 ppm initial NO_x, respectively. Data obtained after subsequent NO_x injections not shown.

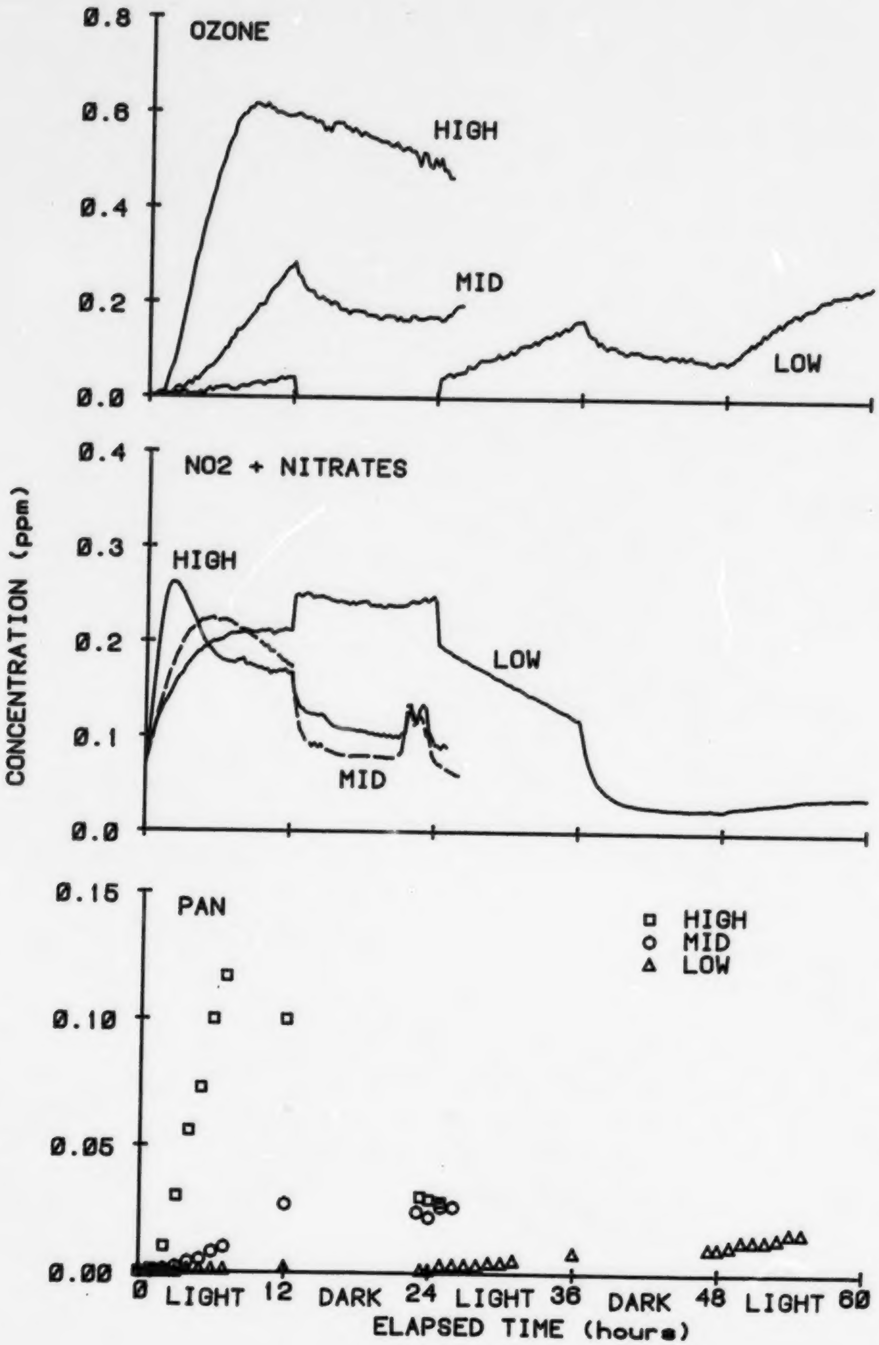

Figure 20. Concentration-time plots for O_3, uncorrected NO_2, and PAN for indoor chamber runs ITC-630, 631 and 637. " Low," "mid," and "high" refer to runs with 1, 2, and 4 ppmC initial surrogate, respectively. Data obtained after subsequent NO_x injections not shown.

the outdoor chamber experiments (see Figures 14 and 15 in Section III.A.8).

However, as shown in Figure 20, the continued formation of O_3 on the third day of the run with the lowest surrogate level (run ITC-637) is somewhat unexpected, since the uncorrected NO_2 concentration-time profile indicates that the initial NO_x should have been consumed by then. This O_3 formation on the third day could be due to a NO_x offgassing effect. Although the results of the acetaldehyde-air irradiations indicate that NO_x offgassing was relatively minor at the beginning of the run (i.e., after the chamber was well flushed), this does not imply that this was necessarily the case after two days of a multi-day surrogate-NO_x-air irradiation. Indeed, the acetaldehyde-air irradiations carried out in the outdoor chamber indicated somewhat higher NO_x offgassing rates when the chamber was not flushed, and this effect may be more important in the relatively smaller indoor chamber.

As was the case for the outdoor chamber irradiations, the addition of NO on subsequent days of the experiments resulted in additional O_3 formation, providing that the amount of NO added was not so high that O_3 formation was suppressed by the presence of large levels of excess NO. For example, Figure 21 compares the results of two surrogate-NO_x-air irradiations (runs ITC-626 and 637) when NO was added on subsequent days. The two runs had approximately the same initial reactant concentrations, and good reproducibility was observed in the first day of the irradiation. In run ITC-626, the amount of NO added was so high (~0.8 ppm) that it completely suppressed O_3 formation. It is interesting to note that after the first two hours following NO addition, the oxidation of NO essentially stopped, indicating a very unreactive mixture. However, when relatively low levels of NO (~0.2 ppm) were added each day for the subsequent three days of the run, significant O_3 formation occurred on each day, though the increase of the O_3 concentrations following each NO injection decreased monotonically each day. This indicated a gradual decrease in the reactivity of the reacting surrogate mixture with time.

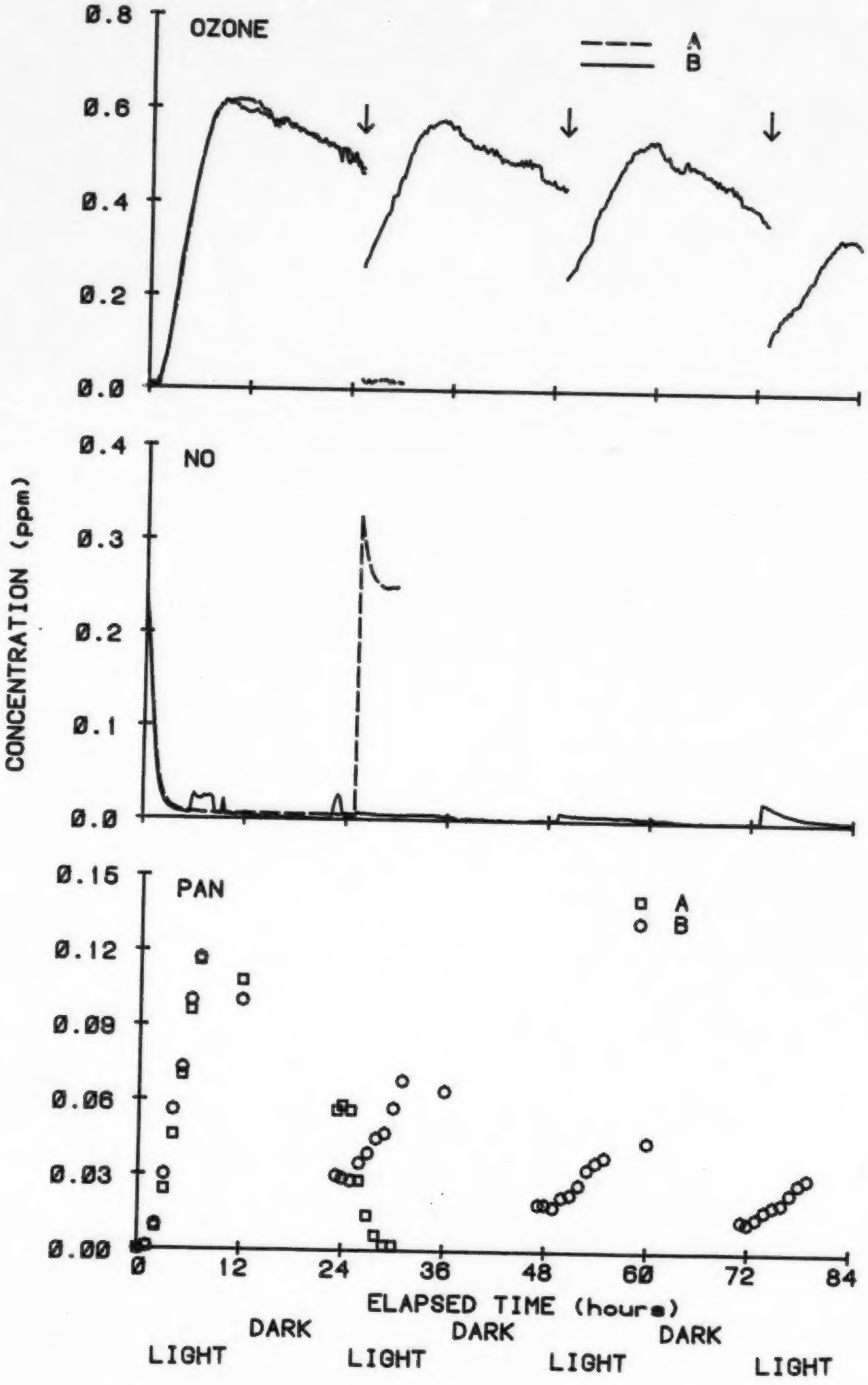

Figure 21. Concentration-time plots for O_3, NO and PAN for indoor chamber runs ITC-626 and 637. Arrows indicate times NO was injected. "A" = run 626, "B" = run 637.

C. Limitations of the Data Set

Although every effort has been made to assure that the data described in this report are as accurate, complete, and well characterized as possible given the scope of effort in this program and other practical constraints, it is important to stress that because of the complexities and uncertainties associated with environmental chamber experiments and some of the analytical techniques employed, there are a number of uncertainties associated with these data which must be taken into account when they are used for model testing purposes. Although most of these limitations or uncertainties have been discussed or alluded to at various places previously in this report, they are summarized in this section for easier reference.

- Chamber effects are unavoidable in environmental chamber experiments, and must be taken into account in computer model simulations. Known chamber effects include chamber radical sources, absorption and offgassing of NO_x and other contaminants, wall destruction of O_3 and perhaps other reactive species, and enhanced rates of heterogeneous reactions such as N_2O_5 hydrolysis, etc. Previous studies carried out in our laboratories have shown that in general chamber effects for Teflon bag reactors appear to be smaller than for other types of environmental chambers, but they also appear to be more variable than in other types of reactors (see, for example Carter et al. 1982, Tuazon et al. 1983, Pitts et al. 1984). A number of control experiments have been carried out in this program to characterize as many of these effects as possible, but complete characterization of all chamber effects is not yet practical (if indeed possible). Among the potentially important chamber effects not well characterized in these experiments include: variable rates of N_2O_5 hydrolysis; heterogeneous formation of HONO from NO_2; radical input rates under conditions where NO_2 levels are rapidly changing; NO_x offgassing rates under conditions applicable to the second and subsequent days in indoor chamber runs (though several experiments aimed at characterizing this quantity for outdoor runs were carried out); adsorption and offgassing of organic contaminants such as polyfunctional oxygenated products which could not be analyzed by the techniques employed.

- Although the results of most chamber characterization experiments carried out in this program were within the range expected for these reactors, in some cases anomalous results were obtained. In particular bag #26, the first reactor employed in the outdoor program, appears to have been contaminated, and experiments carried out using that reactor probably should not be used for model testing purposes (see Section III.A.2). In addition, the reactor employed in the second phase of the indoor experiments appeared to have a high radical source, compared to other indoor Teflon reaction bags. In this case, the results of the characterization runs were reproducible, so runs carried out in this reactor should be usable for model testing purposes, provided that the models use the higher radical source rates characteristic of this reactor.

- As discussed in Section II.C.3 and elsewhere throughout this report, our NO_2 measurements suffer from interference from other nitrogenous species which are converted to NO in the chemiluminescent NO-NO_x detector. These include species such as PAN, organic nitrates, and HNO_3 which are formed in significant yields in these experiments. Except for PAN, most of these species were not routinely monitored, and the extent of interference by HNO_3 is particularly uncertain because of its tendency to be adsorbed and desorbed from the sampling lines. In addition, the efficiency of the interferences by various species seem to be different for the Columbia Scientific Industries, Inc. NO-NO_x analyzer employed in most of the outdoor runs than for the TECO 14-B NO-NO_x analyzer employed in the indoor experiments. Thus, we have no direct measurement of NO_2 levels in these experiments, and the "uncorrected NO_2" data, particularly after the first day when most of the initially present NO_2 has been consumed, are of qualitative utility only.

- As discussed in Section III.A.6, the first series of outdoor chamber runs were plagued by side inequivalency problems, whose cause has not been unambiguously determined. Thus we recommend that data from these runs not be used for model testing purposes, except perhaps with regard to models for chamber effects. The second series of outdoor runs showed much better side equivalency and reproducibility, and these are considered to be much more suitable for modeling.

- As discussed in Section II.C.2, the formaldehyde analysis technique employed in this program did not always obtain reliable results, and

HCHO data should be employed only with caution. Except for a few spurious points, most of the formaldehyde data for the outdoor experiments appear to be usable, in that they indicate concentration-time trends expected based on the known chemistry of the systems studied. However, plots of the formaldehyde data from essentially all of the indoor surrogate-NO_x-air experiments show such large scatter that no concentration-time trends can be discerned. On the other hand, the formaldehyde data in the propene and isobutene runs carried out in the second series of indoor chamber experiments appear to be good, and formaldehyde analysis tests carried out in September of 1983 (between the first and second phase of indoor runs) employing known pressures of formaldehyde vapor injected into the 5800-ℓ evacuable chamber gave results within ~30% of the amount injected. Thus the reason for the problems with the formaldehyde data in the indoor surrogate runs is unknown.

- The dew point hydrometer employed to measure the dew point in the outdoor experiments was frequently not given the maintenance it required, resulting in spurious readings. That data should be ignored in runs where large variations in these readings occurred.

- The NO_2 actinometry measurements made in the outdoor runs measured only the light intensity underneath the chamber, after the sunlight had passed through both the top and the bottom of the chamber. Thus the light intensity within the chamber was probably higher than indicated by these measurements. We estimate that the Teflon film of which the reactor was constructed attenuated the light by at least 10%, with the attenuation becoming greater as the reactor became increasingly well used.

- In some experiments excessive leakage of the outdoor chamber resulted in one of the sides becoming more deflated than the other. When this occurred it was noted in the comments on the data sheets. In such cases, one would expect chamber effects to be greater due to the greater surface/volume ratio, and possibly also some contamination by the outside air. Note that in the outdoor experiments, the O_3, NO and NO_x levels outside the chamber are included along with the data for the run (as "Side 3" data).

- It should be noted that the UV absorption technique used to monitor O_3 in the indoor Teflon chamber experiments is subject to interference by certain organics such as oxygenated aromatics (see, for example, Atkinson et al. 1980) which may be formed in the surrogate-NO_x-air irradiations. Although there is no direct evidence for such interferences in these experiments, they cannot be ruled out.

- Although the indoor chamber experiments have the advantage over the outdoor runs in that there is much less day-to-day variation in temperatures and light intensity, it should be noted that temperature is not totally constant in the indoor runs. In particular, the temperature generally increased by 4-5 C in the first ~15 min after the lights were turned on, and varied by ~±2 C thereafter. This may need to be taken into account in the model calculations. The temperature was recorded at 15 minute intervals for the indoor runs.

In addition to the experimental considerations discussed above, it should be noted that the data obtained in this study certainly do not address all of the data requirements for development and validation of reliable computer models for multi-day effects. For example, this study was carried out using only a single surrogate composition, and no data concerning the effects of changing reactivity of the organics present have been obtained. In addition, the effects of such factors as dilution, entrainment of pollutants from aloft, injection of organics as well as NO_x on subsequent days, etc. have not been addressed in this study. Although the priorities for additional data requirements will become evident only after modeling studies of these and other available data have been carried out, it is clear that additional experimental studies will be required.

However, despite these limitations, we believe this experimental study has been successful, given the overall scope of this program. In particular, good reproducibility has been obtained not only in the indoor chamber experiments (see Figure 21 in Section III.B.5) but also, when lighting and temperature conditions were comparable, in the second phase of the outdoor runs (see Figures 11, 14, and 15 in Section III.A.8). In addition, good precision in the chromatographic, inorganic, and radiometric light intensity were obtained, the actinometry measurements appear to be reasonably accurate, and the results of the chamber characterization runs in the indoor runs and the second phase of the outdoor runs were reasonably reproducible. A number of surrogate-NO_x-air experiments with varying initial hydrocarbon and NO_x have been successfully carried out in both chambers, allowing these effects to be elucidated, at least for the particular surrogate mixture and static reaction conditions employed. Thus we believe the data obtained in this program should allow significant progress to be made towards the goal of the development and validation of reliable computer models for multi-day effects.

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